

CHEMICAL
NEWS

84

JULY-DEC.

1901



LIBRARY
OF THE
UNIVERSITY
OF ILLINOIS

540.5

CN

v.84

~~Chemistry~~



Digitized by the Internet Archive
in 2014

<https://archive.org/details/chemicalnewsjour8419unse>

THE CHEMICAL NEWS, JANUARY 10, 1902.

THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXXIV.—1901.

LONDON:

PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCL.

LONDON:

PRINTED BY EDWIN JOHN DAVEY
6 & 7, CREED LANE, LUDGATE HILL,
E.C.

SUPPLEMENT TO THE CHEMICAL NEWS,

JANUARY 10, 1902.

TRADE "OPTIMUS" MARK.

ESTABLISHED 1852.

MANUFACTURERS OF

PHOTOGRAPHIC APPARATUS

OF EVERY DESCRIPTION.

100 PAGE CATALOGUE POST FREE.

PERKEN, SON, & CO., LTD.,

99, HATTON GARDEN, Holborn viaduct, LONDON.

BROWNING'S SPECTROSCOPES

AND

SPECTROMETERS,

FOR

ANALYTICAL

and RESEARCH WORK.

Price Lists gratis from

JOHN BROWNING,

Manufacturing Optician,

63, STRAND, LONDON, W.C.



OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and purchased.

G. E. MÜLLER, ORME & CO.

(Contractors to His Majesty's Government),

148, HIGH HOLBORN, LONDON, W.C.

Manufacturers and Importers of all kinds of

CHEMICAL & PHYSICAL APPARATUS.

CHEMICALS, Pure and Commercial, in large and small quantities.

CHEMICAL BALANCES.

Colleges, Schools, & Technical Institutions supplied on liberal terms.

SCIENTIFIC GLASS BLOWING from SKETCH a SPECIALITY.

THERMOMETERS, BAROMETERS, AND HYDROMETERS OF EVERY DESCRIPTION. X-RAY ARGON AND HELIUM TUBES.

Sole Makers of Cribb's Condensers, Tyrer-Marsh Arsenic Apparatus, &c.

Catalogues free.

E. GEORGE & SON,
BOOKSELLERS,

151, WHITECHAPEL ROAD, LONDON, E.,

Are OPEN to PURCHASE Complete Sets or short runs of the following:—*Chemical News*, *The Analyst*, *Journal of the Chemical Society*, 1848 to 1870, *Journal of the Society of Chemical Industry*, or the Publications of any other English or Foreign Learned and Scientific Societies.—Libraries Purchased. Catalogues sent on application.



FRIDOLIN GREINER,

NEUHAUS-AM-RENNWEG, GERMANY,

MANUFACTURERS OF CHEMICAL AND PHYSICAL APPARATUS.

SPECIALITIES:—

Chem. Thermometers, Burettes, Glass Wool, Watch Glasses, Flasks, Vials, Plain Tubes, Stoppered Bottles, &c.

Orders from £5 upwards delivered free to house

A. C. COSSOR,

Original Maker of "X" RAY TUBES in England.

FOCUS TUBES giving finest possible definition. IMPROVED TUBE HOLDERS, with arrangement for securing wires to avoid perforation of tube.

All kinds of "X" Ray Apparatus. Mercury Pumps, Screens, Spark Gaps, &c. Applications for Price Lists invited.

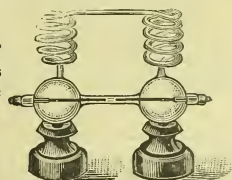
Glass Blowing.

All kinds of Experimental Glass Blowing carried out for Scientific Men, Laboratories, &c.

INVENTORS' IDEAS WORKED OUT AS PER INSTRUCTIONS.

COSSOR,

54, Farringdon Road, E.C.



Hittorf's Tube showing the resistance of the dark space.

ACETONE.

JOHS. OSWALDOWSKI.
!ALTONA, near HAMBURG.

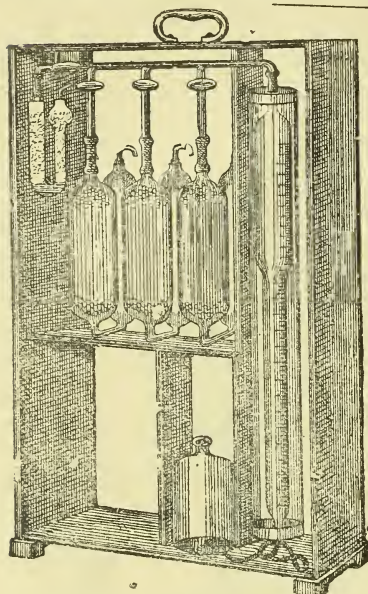
FRED^K. JACKSON & CO.

(Late MOTTERSHEAD & CO.),

14, Cross Street, MANCHESTER.

GOODS ENTRANCE—10, Half Moon Street.

TELEGRAPHIC ADDRESS—Apparatus, Manchester.



ORSAT-MUENCKE'S GAS ANALYSIS APPARATUS.

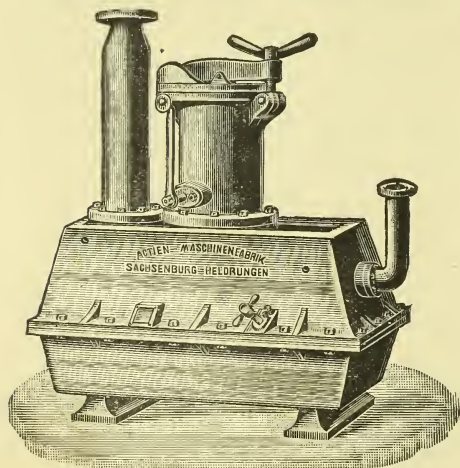
*Balances, General Chemical Apparatus,
and Pure Chemicals*

**HEMPEL'S AND ORSAT-MUENCKE'S
GAS ANALYSIS APPARATUS.**

**THE LONDON GAS REFEREES' APPARATUS
FOR TESTING COAL-GAS.**

GAS BURETTES OF VARIOUS KINDS.

ILLUSTRATED PRICE LISTS FREE ON APPLICATION.



**Sachsenburger Machine Manuf'g
Joint Stock Company and
Iron Foundry,**

**Of Sachsenburg-Heldrungen on the
Kyffhaeuser (Germany).**

*FURNACES FOR BURNING SULPHUR and
AIR-PUMPS, &c.*

APPARATUS FOR THE PRODUCTION OF SO₂.

Numerous first-class HOME and FOREIGN References.

Up to now about 1500 Apparatus Sold.

Agents conversant with the Business wanted.

SCIENCE AND ART EXAMS.

LONDON AND SOUTH KENSINGTON.

ORAL or CORRESPONDENCE Tuition by

Specialist Tutors.

New and Perfected System of Correspondence Tuition.
Worksheets a Speciality, saving Time and Trouble.

Address—

JOHN GIBSON, M.A.

**24, Chancery Lane,
W.C.**

HANDBOOK OF PATENT LAW.

BY
W. P. THOMPSON, C.E., F.C.S., &c.

The above well known work has just been thoroughly revised, and the large number of alterations made since 1896 in Continental and Foreign Patent Laws have been summarised in an Addendum. Price complete, 2s. 6d.

W. P. THOMPSON & CO., Patent Agents,
6, Lord Street, Liverpool; 322, High Holborn, London, W.C.

THE CHEMICAL NEWS.

VOLUME LXXXIV.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2171.—JULY 5, 1901.

EUROPIUM: A NEW ELEMENT.

By EUG. DEMARCAV.

In 1885 Sir William Crookes (*Phil. Trans.*, vol. clxxvi., p. 691), during his beautiful researches on electric phosphorescence *in vacuo*, noticed a band which he attributed to samarium, and which by reason of its disappearance in presence of lime, and from certain other peculiarities, he called the "anomalous line." Later (*Journ. Chem. Soc.*, 1889, President's Address), he distinguished this, together with a large number of other bands, as belonging each to a special meta element. The hypothetical meta element corresponding to the anomalous line he called S_a . M. Lecoq de Boisbaudran, in the course of his important researches on phosphorescence, confirmed the above statements with regard to this anomalous line.

In 1892 M. de Boisbaudran (*Comptes Rendus*, 1892, p. 575), described a spectrum consisting of three brilliant blue lines, discovered in the spark spectrum of samarium. These three lines can be reinforced by suitable fractionation. He therefore concluded that they correspond to a particular element Z_e . About the same time he also drew attention (*Comptes Rendus*, 1893, I., pp. 671–674; II., 199), to a particular band in the reversal spectrum of samarium, which apparently corresponds to the anomalous line, and is considerably reinforced in nitric solution. M. de Boisbaudran, without forming very precise conclusions, inclined to the idea that this line was due to a particular element Z_e .

In 1896 (*Comptes Rendus*, vol. cxvii., p. 728), I discovered the presence of an element intermediate between gadolinium and samarium characterised by several strong lines in the violet and ultra-violet. In 1900 (*Comptes Rendus*, cxxx., p. 1469), I showed that this new element was identical with de Boisbaudran's Z_e , and that Crookes's anomalous band was due to the same substance (see Note), as well as the reversal line Z_e , and various other reversal lines not yet identified. I found also that this new element had a special absorption spectrum previously unnoticed. I may add that it has not been possible to carry the fractionations far enough to affirm absolutely that all these properties correspond to the same substance. Since that period, by a long series of fractionations with magnesium nitrate, I have been able to accumulate a considerable quantity of this element, and so able to confirm its various characteristics, and the following spectra:—Reversal, absorption, electric phosphorescence of the sulphate in vacuum (anomalous line), of the sulphate, together with calcium sulphate or gadolinium, which accompanies it in nearly all cases. The properties remain sensibly constant, and evidently characterise the same element. The purity of several grammes of the new oxide was sufficient to show no samarium lines and mere traces of the gadolinium lines.

When traces of calcium sulphate are added to this pure product a brilliant phosphorescent spectrum is produced, in which the anomalous line appears. (See Note).

This spectrum contains three principal bands:—

$\lambda = 609$ about.	Very strong.
$\lambda = 576$ „	Wide and well marked.
$\lambda = 593$ „	Strong, very wide.

The degree of calcination of the mixed sulphate causes a variation in the appearance and the size of the bands. The strongest apparently is converted into a double line when the sulphates are raised to a very high temperature. The spectrum of samarium (especially the red line) was quite invisible. In the gadolinium sulphate the most brilliant lines formed an analogous system, but more complicated. With strongly calcined alumina the spectrum is formed of very brilliant thin lines. I have not yet been able to measure the lines of these spectra. These apparently contradictory results of Crookes and de Boisbaudran are due, I think, to the very small proportions of $\Sigma-Z_e$ contained in their material, and that the calcium and gadolinium present reinforced the samarium spectrum rather than the other.

I propose the name europium for the new element, with symbol Eu and atomic weight 151 (approx.).

Below is a list of the strongest lines in the spectrum of europium comprised between $\lambda = 500$ and $\lambda = 350$. The strongest are in the list of the samarium lines given by Exner and Haschek. I repeat that in my spectrum the true samarium lines were absolutely wanting, and the strongest gadolinium lines only just visible:—

λ .	Strength.	λ .	Strength.
4662.6	12	3819.5	15
4627.8	13	3815.2	5
4594.5	14	3817.4	5
4435.8	16	3781.1	5
4355.5	7	3741.0	5
4205.4	16	3724.5	13
4173.2	5	3688.3	11
4130.0	15.5	3629.9	7
4062.3	5	3622.5	5
4057.8	6	3616.1	5
4017.6	6	3570.0	6
4012.7	5	3549.7	7
4011.8	7		
3988.4	6 (wide)		
3972.0	15		
3943.2	7	3547.6	5
3930.7	15	3543.9	9
3907.2	14	3541.2	5
3877.4	5	3530.8	6
3861.3	6	3520.6	12
3854.7	5	3530.8	5

Near a strong more refrangible ray of Gd.

Besides the above mentioned lines which I believe to belong definitely to europium are a very large number of weaker lines, the greater portion being extremely feeble. Much greater doubt naturally exists as to the origin of these lines, which nevertheless disappear from the spectrum if the europium is not very pure. I believe them to belong to this element, though it is possible to suppose that they belong to an unknown element present in minute quantities, even relatively to europium, which is itself so rare. Further investigation is necessary on this matter.

For the lines of the reversal spectrum and the absorption spectrum of europium salts I must refer to my previous paper already quoted.—*Comptes Rendus*, No. 24, June 17th, 1901, vol. cxxxii.

[NOTE.—It is necessary for me to make one or two corrections to the paper of M. Demarçay.

1. I have never admitted that the body called by M. de Boisbaudran Z_6 is the same body which gives my "anomalous line." Indeed, I have good reason to think they are quite different. The line given by M. de Boisbaudran's Z_6 is broad and indistinct at the edges, while the "anomalous line" is absolutely sharp and narrow, like a gas line. Also, their refrangibilities are not identical. The same remarks will apply to the body described by M. Demarçay in his 1900 paper.

2. Fifteen years ago I stated (*Proc. Roy. Soc.*, vol xl., p. 505) that a little calcium sulphate entirely suppressed the "anomalous line."—W. CROOKES].

A FEW CONSIDERATIONS ON THE ATOMIC WEIGHTS.

By Dr. T. L. PHIPSON.

DURING the last half century we have seen a great number of laborious experiments, made with the view of determining what are termed "the true atomic weights" of the elements. In future this kind of labour will be saved to a great extent by the perusal of the remarkable work of Gustavus Hinrichs, M.D., LL.D., Professor of Chemistry in the St. Louis College of Pharmacy.

Dr. Hinrichs has devoted a great portion of his studious life to this subject, and we have now in his work, published in 1894, and entitled "The True Atomic Weights of the Chemical Elements," the results of his long and valuable experience.

To an English chemist who, by a stroke of genius, gave us what is universally known as "the law of Prout," our science owes a great deal, and it has been part of Prof. Hinrichs's task to show not only to what an extent chemical science is indebted to Dr. Prout, but how vain have been all the efforts made with the view of proving his law incorrect.

Whilst admiring the perseverance of such ambitious men as the late M. Stas, of Brussels, and his various disciples in England and Germany, Hinrichs points out very clearly that all these laborious determinations of atomic weights of well known elements, when analysed by the aid of one of the simplest of mathematical formulæ, show in favour of Dr. Prout's hypothesis, instead of against it, and tend towards the theory of the "Unity of Matter."

By the severe criticism given in this work of certain results published by Ostwald, Richards, and others, and by pointing out better results previously obtained by Berzelius, Struve, Marchand, Dumas, and Marignac, he will, doubtless, have opened the eyes of the younger generation of scientific chemists who may some day feel inclined to undertake researches of this description. Moreover, the absurdity of replacing the old round numbers of the text-books by these numbers and a fraction,

as has been done recently by some German periodicals, is now thoroughly brought to light.

It is painful to all those who have at heart the welfare of chemical science to find a certain number of blind enthusiasts attempting to substitute the uncertain figures obtained experimentally by Stas for those which the true scientist knows must be nearest the truth. For a long series of years the practical analyst in Great Britain has been satisfied with the small and mostly whole numbers derived from the law of Prout. Whilst Continental chemists adopted $O=100$, we in England made $H=1$ (and for all practical purposes that is quite sufficient). Now, and for many years past, foreign nations have followed our example in this respect.

It should not be forgotten that, in this world, absolute perfection is denied to us, though we naturally strive to approach it as nearly as possible. The laborious efforts of Stas and his followers have, unfortunately, done harm to science, as Prof. Hinrichs clearly demonstrates in the admirable work which I have named.

It is impossible here to quote detached passages; it must be read as a whole; but it may be stated that the upshot of this truly wonderful book is to prove that the figures published by Stas, when considered from a mathematical point of view, are of no value to the science of chemistry.

With regard to the fact that the law of Prout points to a confirmation of the theory of the "Unity of Matter," this is to be gleaned already from the excellent "Elements of Chemistry," published in 1855, by the late Dr. Gregory, Professor of Chemistry in the University of Edinburgh. When I published in 1886 my "Outlines of a New Atomic Theory," recently reprinted as an appendix to my little work "Researches on the Earth's Atmosphere," I was not aware that some twenty years or more previously similar views had been held by Prof. Gustavus Hinrichs. He imagined the existence of a body which would have half the atomic weight of H, and called it "pantogen," declaring at the same time that with such a substance (which may some day be discovered), the law of Prout will remain as perfect as Newton's theory of gravitation.

In my little sketch I have merely endeavoured to demonstrate that the atoms of all substances are of the same size and same weight, and that difference of properties of various substances is owing to their "phlogiston," that is, the distance (space, energy), at which the atoms are placed. H being the substance in which the atoms are at the greatest distance—which has the greatest amount of "phlogiston"—is also the most energetic body hitherto discovered. C, H, N, and O are, of all the elements, those which contain the most "phlogiston," possess the greatest energy and nearest approach to vitality; hence they form the whole of organic nature.

In the last annual address to the Paris Academy, by the President, these views are alluded to as likely to lead to new and interesting developments.

POTASSIUM PERSELENATE.*

(PRELIMINARY NOTE).

By L. M. DENNIS and O. W. BROWN.

POTASSIUM perselenate was prepared by the electrolysis of a saturated solution of potassium selenate containing a little free selenic acid. This solution was placed in a 150 c.c. beaker, and the anode, a platinum plate of about 15 sq. c.m. surface, was introduced into it. The cathode, a piece of platinum foil, was contained in a small porous cup of about 75 c.c. capacity which was suspended in the solution. This porous cup was filled with a dilute solu-

* The experimental work herein described was performed by Mr. Brown in the spring of 1898. It has been impossible to resume the work until recently, but it is hoped that the investigation may soon be carried to completion.

tion of selenic acid. The beaker was placed in a freezing-mixture, and a current varying from 2.5 to 3 amperes was passed through the solution. The temperature in the outer cell averaged about 4° C.

After the action of the current had continued for some hours, a white substance began to appear in the neighbourhood of the anode, its formation being accompanied by an increase in the resistance of the cell. After considerable of the solid had separated, the process was interrupted, the solution in the beaker was decanted, and the substance dried on a porous plate. It was then placed in a desiccator containing phosphorus pentoxide, and this was placed upon ice.

The complete analysis of the substance was not made at the time, but merely the available oxygen was determined, this being done, first by adding oxalic acid in excess, and determining the excess by means of potassium permanganate, and second, by adding ammonium ferrous sulphate in excess, and titrating this excess in the same manner.

The two methods gave agreeing results, for when used on a sample of potassium selenate containing a small amount of perselenate, oxalic acid, and potassium permanganate, showed 2.41 per cent of KSeO_4 , while the ammonium ferrous sulphate method gave 2.42 per cent.

Potassium perselenate was not obtained free from selenate, the highest percentage of perselenate in the product being 74.44.

Potassium perselenate, when hot, oxidises manganese dioxide to potassium permanganate, quickly oxidises ferrous sulphate in the cold, and acts similarly upon thallous sulphate. An aqueous solution of the salt gives off oxygen when warmed.—*Journal of the American Chemical Society*, vol. xxiii., No. 5.

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.*

By H. L. WELLS and F. J. METZGER.

In a recent number of a German periodical (*Ztschr. Angew. Chem.*, 1901, 165), appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that, upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present (see Ruegenberger and Smith, *Journ. Amer. Chem. Soc.*, xxii., 772), washed the residue, and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid added, the liquid carefully evaporated, and the residue ignited over a

Bunsen burner. Then another portion of silica was added, and the operation repeated. The results are shown in the following table:—

	Taken.		Tungsten trioxide found after	
	Tungsten trioxide.	Silica.	First operation.	Second operation.
	Grm.	Grm.	Grm.	Grm.
I.	0.1928	0.2	0.1927	0.1928
II.	0.2097	0.2	0.2097	0.2096
III.	0.2100	0.2	0.2099	0.2100
IV.	0.1999	0.2	0.2000	0.1998

The greatest error found in these experiments is 0.0001 grm., and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results. It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used:—

	Taken.		Tungsten trioxide found.
	Tungsten trioxide.	Silica.	
	Grm.	Grm.	Grm.
	0.1983	0.2	0.1983
	0.2102	0.2	0.2100
	0.2106	0.2	0.2105
	0.1996	0.2	0.1994

In these experiments, the greatest error, 0.0002 grm., is well within reasonable limits; hence, it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also, the tungstic acid was ignited by the Bunsen flame only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced, it volatilises to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating some of the substance (which showed no loss of weight over the Bunsen burner), over the blast-lamp in a platinum crucible:—

Taken	Ignited for two minutes	Weight of tungsten trioxide.	Loss.
		Grm.	Grm.
.. .. .		0.3007	—
.. .. .		0.2978	0.0029
.. .. .	again..	0.2962	0.0016
" " " "	"	0.2946	0.0016
" " " "	"	0.2932	0.0014
" " " "	"	0.2924	0.0008
" " " "	"	0.2916	0.0008
" " " "	"	0.2906	0.0010
" " five "	"	0.2872	0.0034
Total loss ..			0.0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent., while in another experiment 0.1955 grm. of tungstic acid lost over 7 per cent after heating with the blast-lamp for twenty

* Contribution from the Sheffield Laboratory of Yale University. From the *Journal of the American Chemical Society*, xxiii., No. 5.

minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

PART I.—THE CIRCUMSTANCES OF THE FALL OF THE STONES.

ON January 25th, 1899, at 7 54 a.m., a loud noise as of an explosion was heard at the settlement of Zomba, British Central Africa, and for many miles around; almost simultaneously therewith, several small stones were seen to reach the earth in the neighbourhood of Zomba and were collected by the observers of their fall.

Mr. Alfred Sharpe, C.B., His Majesty's Commissioner and Consul-General for the Protectorate of British Central Africa, Mr. J. F. Cunningham, Secretary to the Administration, and Mr. J. McClounie, the Acting Collector of Revenues, on hearing the detonation, surmised that it had an origin in the entry of a meteorite into the earth's atmosphere, and with praiseworthy zeal and energy at once proceeded to collect, by aid of the telegraph and by personal interviews with the witnesses, all the reliable evidence that could be obtained relative to so extraordinary a phenomenon. A Report, embodying this information and the notes made by Mr. Cunningham and Mr. McClounie, was sent by Mr. Sharpe to the British Museum; four of the stones, generously presented by Mr. Sharpe, Mr. Cunningham, and Mr. McClounie, were forwarded at the same time for scientific examination, and for subsequent preservation in the Meteorite Collection of the Museum.

The details given in the Report may be classified as follows:—

Luminous Meteor and Trail.

(Zomba). "There being much cloud at the time, nothing was visible to indicate that a meteorite had entered the earth's atmosphere."

(Blantyre). "A native named Bwanali, who was sitting in the open near the Government buildings, saw, a little before 8 a.m., a star of exceptional brilliancy pass across the sky in the direction of Lake Shirwa (roughly, west to east)." "A native captao in the employment of Mr. James Lindsay makes a similar statement, and adds—it left a trail or tail behind it."

(Chiromo). "Mr. H. C. McDonald telegraphed that several natives saw the star and smoke. They stated that it appeared to pass over Cholo."

(Fort Johnston). "Mr. O. C. Ockenden, the Acting British Vice-Consul, telegraphed that the meteorite had been seen from Fort Johnston."

(Chengali's village). "Sergeant-Major Bandawe, of the British Central African Rifles, who was on his way to Zomba, saw the meteor when he was at Chengali's village to the West of Lake Pamalombe. It left a trail, and exploded in the direction of Chikala."

Owing to the cloudy state of the sky the luminous meteor was thus seen from only a small number of places,

and presumably for only small portions of its path. It must have been far above the clouds, for it was seen from places 130 miles apart. The meteor appears to have been travelling in an approximately easterly direction, and was seen to explode when near a line drawn from Lake Pamalombe to Chikala.

Detonation.

(a). Places at which it was heard.

(Top of Mt. Zomba). Mr. Sharpe says:—"I heard one very loud report."

(Zomba). "Mr. Cunningham says:—"There was heard a crash like thunder."

(Blantyre). "The native Bwanali heard an explosion like a crash of thunder. A native captao in the employment of Mr. James Lindsay makes a similar statement."

(Chikwawa). "Mr. J. O. Bowhill, the Judicial Officer at Chikwawa, heard the explosion as he was standing near his house. It seemed to him to come from the direction of Blantyre."

(Katunga). "Mr. C. B. Vertue, the Agent of the African Lakes Company, made inquiries, and states that the explosion was heard by Muri (a native servant), 'James' and Mgano (captaos), Njeresa and Mpeni (natives in charge of cattle).

"A native from Katunga's village came in to Chikwawa and told the Collector of Revenues that the explosion had been heard in that village."

(Chiromo). "Mr. H. C. McDonald telegraphed that several natives heard the explosion."

(Fort Johnston). "Mr. O. C. Ockenden telegraphed that the explosion had been heard at Fort Johnston."

As far as could be ascertained, neither the luminous meteor nor the detonation had been remarked by any one at Kota-Kota, Nkata, or Karonga, places which are north of Fort Johnston, and lie on the western shore of Lake Nyasa; they are in telegraphic connection with Zomba.

(b). Character of the Detonation.

The character of the detonation as heard by an observer would vary to some extent according to his situation.

(Zomba). Mr. J. F. Cunningham says:—"I heard a crash like thunder, the reverberations lasting for a few minutes afterwards. When I heard it, I suspected what it was, but thought it might possibly be a dynamite explosion on the road to the new Residency, where I knew the Road-Engineer, Mr. William Fletcher, and a party of men were at work. I sent an inquiry to Mr. Fletcher, and he sent back word that he also had heard the explosion, but that it had not occurred on the Road."

Mr. J. McClounie says:—"The loud report had the precision of a cannon. I was indoors at the time, but instantly rushed out to see what had happened. My attention was drawn towards the east by the continuous rolling noise. The natives also were looking in an easterly direction."

(Top of Mount Zomba). This mountain rises to a height of 6000 feet above the sea, and is on the western side of the settlement, which is itself 2900 feet above the sea. Mr. Sharpe says:—"I heard one very loud report; then for some two minutes a long rumbling or buzzing noise, gradually getting fainter and fainter; I should not call it reverberations."

(Kuntamba's village). "The chief Kuntamba, at his village about three miles from the Residency, to the west of the road to Domasi, heard a noise like thunder."

(Blantyre). "The native Bwanali heard an explosion like a crash of thunder."

The detonation was thus a single one; at Blantyre and about 50 miles away in the villages north-east of Zomba it was as loud as thunder; it was heard also at Chiromo, about 90 miles south of the settlement of Zomba, and also beyond Fort Johnston, which is at a

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

distance of 70 miles to the north of Zomba; to the observers at Zomba itself the sound seemed to come from the east.

Fall of Stones.

About an hour after the detonation had been heard, news reached the Residency that several stones had fallen in native villages on the eastern slopes of Mount Zomba. As many as ten were ascertained to have been found, and these have been preserved; only those stones were discovered which fell near to people or houses, and possibly they form only a small proportion of those which actually reached the earth.

The following is the history of the individual stones:—

Stone No. 1. Weight 2 ozs. 57 grms.). Fell at Kuntamba's village, about three miles from the Residency, to the west of the road going to Domasi. The chief Kuntamba gave the following account to Mr. Cunningham:—"This morning I was standing near my house when I heard something fall on the rock there" (pointing to a fairly level slab of granite, measuring 20 feet by 12 feet, near his house). "Immediately after, I heard a noise like thunder. I went to the rock and saw where a stone had fallen, and I picked up some small bits."

Mr. Cunningham adds:—"There was a large crowd of the village people present when the chief told me this, and two of them, Matendu and Laici, personally vouched for its accuracy. The fragment has only a small portion of outer crust. It is the largest of the pieces found at this spot."

Stone No. 2. Weight 4½ ozs. (128 grms.). Fell at Kumpamba's village, 3 miles from the Residency along the Domasi road. The fall was witnessed by the chief and others. It is the smallest of the completely encrusted stones.

Stone No. 3. Weight 1 lb. 3 ozs. (539 grms.). It was seen by a native to fall on the outskirts of the last-mentioned village. It is incomplete, a large piece having been broken off through impact against a stone when it fell. Presented to the British Museum by Mr. McClounie.

Stone No. 4. Weight 3 lbs. 5 ozs. (1502 grms.). Fell on the border of a new garden on the verge of the forest about 400 yards to the south of the Likangala River, near Chiropa's village. A native was hoeing in the garden when the stone fell. The place was stony, and a corner of the meteoric stone was chipped off by the fall.

Stone No. 5. Weight 12½ ozs. (354 grms.). Fell at Kampunga's village on Buchanan's Estate. "It was about noon when we (Mr. Ravenor and Mr. Cox) got to Kampunga's village (to inquire about the stone reported by Mr. Cunningham to have fallen there). We found the village people squatting round the stone in a circle, discussing the 'miracle' as they called it. No one had touched or approached the stone, and when we arrived it was still lying where it had fallen. The story of its advent was given as follows:—'A woman was pounding corn under a tree, within about ten yards of her hut, when the stone fell. The whole village heard the detonation immediately afterwards, and gathered to where the woman was standing to view the stone. They were afraid of it, thinking it enchanted, and they sat at a distance round it, each giving a version of its probable origin and meaning.' It fell on hard ground, but, as there were no rocks about, I (Mr. Ravenor) was able to dig it up complete. It is covered with crust."

Stone No. 6. Weight 5 lbs. 12½ ozs. (2622 grms.). Fell to the south of the Likangala River, to the west of Stone No. 4. It is the largest stone found, is completely encrusted, and has the usual pittings.

Stone No. 7. Weight 1 lb. 13 ozs. (822 grms.). Fell at Chope's village, near Songani. It is probably

only part of the fallen stone, for one large surface is not encrusted. Presented by Mr. Cunningham to the British Museum.

Stone No. 8. Weight 1 lb. 6½ ozs. (638 grms.). Fell at Chirunga's village, two miles from the Residency, near the Domasi road. The side shown by a photograph of the stone is completely covered with crust.

Stones Nos. 9 and 10. Weights 14½ ozs. (411 grms.) and 1 lb. 1 oz. (482 grms.), respectively. Both of them fell at Kanyama's village, and have been presented by Mr. Sharpe to the British Museum; they are almost completely encrusted stones. "Several people heard them crashing through the trees, and after a search found first one stone, and, later on, the other."

Mr. McClounie says that one small stone in its fall cut a twig from the branch of a tree; this was two miles from Zomba, off the Liwonde road; several of the other pieces were picked up at or near this place.

As the meteorite travelled in a more or less easterly direction and reached the ground only a short distance from Zomba, and the detonation seemed to the observers of Zomba itself to come from the East, it follows that the detonation is really a consequence of the break-up of the meteorite, and not, as has been sometimes suggested, due to the rush of air into the vacuum left behind the meteorite during its flight.

Area of Distribution of the Stones.

Mr. McClounie says:—"As far as I know at present the area over which the stones have fallen is about 9 miles long and 3 miles wide. Whether any fell outside this area may never be known." (The positions of the stones as indicated in a map, Plate I., must be only approximate).

The dimensions thus assigned by Mr. McClounie are exactly identical with those of the area over which the stones were distributed in the case of the meteoritic fall at Knyahinya, Hungary, on June 9th, 1866. The area of distribution of the stones, in the case of a meteoritic shower, has rarely been found to measure more than ten miles by three.

The two heaviest stones, Nos. 6 and 4, weighing respectively 5 lbs. 12½ ozs. and 3 lbs. 5 ozs., were found at the southern end of this area. The next largest, No. 7, still weighing 1 lb. 13 ozs., and probably not more than half of the stone which fell, was at the northern end of the area, and not far from the smallest completely encrusted stone, No. 2, weighing 4½ ozs.; the complete stone, No. 7, may have really been the largest which fell. Stones Nos. 9 and 10, weighing respectively 14½ ozs. and 1 lb. 1 oz., were also found north of the smallest stone.

The area of distribution on the earth's surface of the stones of a large meteoritic shower is usually, not always, elongated in the direction of flight of the luminous meteor, and the stones are generally distributed within this area approximately according to size, the larger ones being near the end towards which the meteor's flight was directed. A distribution precisely according to size would be a necessary result of the resistance of the air on the individuals of an at first closely packed swarm of similar meteoric stones moving through the earth's atmosphere in a direction inclined to the vertical, if each stone remain unbroken during its flight. But an admixture of sizes may result in various ways. For instance, a stone may be broken up into scattered unequal fragments at a point in its passage through the atmosphere such that the subsequent path of the fragments is not long enough for the differentiating effect of the resistance of the air to render of no moment their initial scattering in various directions.

Having regard to such considerations, it will be seen that the number of stones found at Zomba is too small, and the sizes are too intermingled to admit of any sound inference as to the direction of the meteor's path from a mere study of the distribution of the fallen material, but the distribution, especially if No 7 was really the largest

stone, is not inconsistent with the direction suggested by the observations already referred to. It seems likely that the stones resulted from the breaking up of a single mass within the earth's atmosphere; there was only one detonation, and presumably only one important epoch of fracture; as the stones are completely encrusted, the scattering of the fragments must have taken place at a point where their velocity was high enough to cause superficial heating to a high temperature. As there is no mention, in the Report, of deep penetration of the ground, it is probable that the velocity was comparatively small at the time of impact on the earth's surface.

Material of the Stones.

It may be added that the material of the stones was observed to be unlike that of any of the rocks of the district, and that the specific gravity of two of the stones was determined by Mr. T. J. Binnie, Acting Chief Surveyor, to be 3.5, which is much higher than that of any of the Zomba rocks; further, Mr. McClounie noticed the numerous metallic particles glittering on the fractured surface, and proved that the material has a directive action on a compass-needle.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

MESSRS. Jerdan, Blake, Eyre, and Shutt were formally admitted Fellows of the Society.

The following certificates were read for the first time:—Thomas Thorne Baker, 28, Church Road, Forest Hill, S.E.; Edwin Hobson, 3, Oxford Road, Liscard, Cheshire; Charles Harold Johnson, Beaumont, Northcote, Melbourne, Victoria, Australia; Edward Hall Miller, Common Hall, Hadleigh, Essex; Herbert Simpson Newbould, Trinity Hall, Cambridge; Allan Sandford, Market Place, Ulverton.

The PRESIDENT announced that Dr. Armstrong had undertaken to deliver the Frankland Memorial Lecture on Thursday, October 31st, 1901.

ADDRESS TO GLASGOW UNIVERSITY.

The following Address was presented to the University of Glasgow on the occasion of the four hundred and fiftieth anniversary of its foundation:—

"The Chemical Society, as representing Chemical Science in the United Kingdom, desires to congratulate the University of Glasgow on the celebration of the Four Hundred and Fiftieth Anniversary of its foundation.

The Chemical Society recalls with pride the fact that Members of the University of Glasgow have been most distinguished Fellows, and have contributed by their labours, some of which are among the classics of our Science, to the development of chemical learning.

"Thomas Graham, one of the Founders of our Society and our first President, was the most illustrious of the pupils of Thomas Thomson, whose name is honourably connected with Chemistry as head of one of the first Schools of Practical Chemistry established in this Kingdom, a school which he inaugurated within your walls.

"Thomas Anderson, an honoured name with you as a teacher, who was among the earliest to cultivate with an energy and zeal eminently characteristic the newly developed domain of Organic Chemistry, was for many years one of the most active of our Fellows.

"We sincerely trust that your University may continue

to flourish in the future as in the past, and that its efforts to foster and promote the Science which we represent may be as successful in the years to come as they have been since the days of Black.

J. EMERSON REYNOLDS, President.
WILLIAM A. TILDEN, Treasurer.
WYNDHAM R. DUNSTAN,
ALEXANDER SCOTT,
RAPHAEL MELDOLA, } Secretaries."

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Ormsby Gore Adams, Guy Ashwell, Thomas Aspinall, William George Aston, Hubert Haigh Barker, Edwin Sloper Beaven, Fred Bedford, Joseph Samuel Bridges, B.Sc., Arthur Crabtree, George Dean, M.A., Thomas H. J. Eling, B.A., Edward K. Hanson, B.A., Frederick Thomas Harry, Edward Horton, Christopher G. Kiddell, B.A., Robert Tabor Lattey, B.A., Adolf L. F. Lehmann, B.Sc., Ph.D., William Lowson, B.Sc., F. G. Macdonald, Daniel McLaren, B.Sc., Frank Oram, John Powell, B.Sc., John Edward Purvis, M.A., James Bertram Russell, B.Sc., Thomas Sandford, Samuel Edward Sheppard, Gerald T. S. Sichel, Andrew Biggam Smith, John Davidson Spence, Arnold Rowsby Tankard, George William G. Tatam, William Arthur Whitton, James Whittle, and Duncan R. Wilson, B.A.

Of the following papers, those marked * were read:—

*105. "The Direct Union of Carbon and Hydrogen." Part II. By W. A. BONE and D. S. JERDAN.

The authors have already shown (*Trans.*, 1897, lxxi., 41) that carbon and hydrogen combine at 1200°, forming a saturated hydrocarbon; and also that when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, a saturated hydrocarbon is produced in addition to acetylene, the formation of each continuing until a definite equilibrium between acetylene, the saturated hydrocarbon, hydrogen, and carbon vapour is established. It was then provisionally assumed that the saturated hydrocarbon produced both at 1200° and in the arc is methane.

Further experiments have been made in which the saturated hydrocarbons in question have been separated from the large excess of hydrogen (by means of palladium), and also, in the case of the arc gases, from the acetylene simultaneously produced. Analyses of the residual saturated hydrocarbons, mixed with whatever nitrogen was contained in the original hydrogen employed, have shown that whereas the gas obtained by the direct action of hydrogen upon solid carbon at 1200° consists of methane only, the saturated hydrocarbons produced in the arc consist of methane with one of its homologues, which further investigation has shown to be ethane.

The authors are able to show further that in the arc methane and ethane are produced simultaneously, and at rates which bear a constant ratio to one another throughout an experiment, until a definite equilibrium is reached. By calculation from the results of the previous experiments, interpreted in the light of later work, the proportions between the various hydrocarbons and hydrogen when this equilibrium is attained are shown to be:—

Hydrogen	90—91 per cent
Acetylene	8—9 "
Methane	1.25 "
Ethane	0.25 "

*106. "Ammonium and Other Imidosulphites." By E. DIVERS and M. OGAWA.

The authors have already called attention to the occurrence of ammonium imidosulphite amongst the products of the decomposition of ammonium amidosulphite, and have given some account of the salt (*Proc.*, 1900, xvi., 113). They now separate it by dissolving it out with warm 90 per cent alcohol, after having used 95 per cent alcohol to extract some other crystalline matter and the red substance. By

working in this way, the imidosulphite is obtained at once almost pure, requiring only to be washed with alcohol. It forms minute, very thin, glistening prisms, somewhat deliquescent, neutral to litmus, and of mild sulphurous taste. Heated in the dry state, most of it decomposes, but a little occurs in the sublimate along with pyrosulphite. The residue left on heating it up to 150° consists of sulphur, sulphate, and imidosulphate. The salt is very soluble in water, and slowly decomposes in solution. Boiled with hydrochloric acid, it yields sulphur, sulphur dioxide, and amidosulphuric acid, the sulphur and sulphur dioxide representing, no doubt, decomposed thiosulphate, $2\text{NH}(\text{SO}_2\text{NH}_4)_2 + \text{OH}_2 = 2\text{NH}_2\text{SO}_3\text{NH}_4 + \text{S}_2\text{O}_3(\text{NH}_4)_2$. Ammonium imidosulphite gives a barium precipitate soluble in hydrochloric acid. Potassium imidosulphite and barium ammonium imidosulphite have been prepared, and are crystalline soluble salts.

*107. "Nitrilosulphates." By E. DIVERS and T. HAGA. Ammonium nitrilosulphate cannot be obtained by the sulphonation of ammonia, for the imidosulphate which is the product of the union of sulphur trioxide with ammonia is decomposed by heat only at a very high temperature, and then is radically broken up without giving any nitrilosulphate. The sulphonation of a nitrite first into hydrox-imidosulphate and then into the nitrile is therefore the only way open. The ammonium and potassium salts were obtained by Frey (1845), and a potassium sodium salt, $\text{SO}_3\text{Na}\cdot\text{N}(\text{SO}_3\text{K})_2$, by Raschig (1887). The ammonium salt, as it has the composition of $4\text{NH}_3 + 3\text{SO}_3$, is a very interesting salt, the existence of which had been forgotten. Sodium nitrilosulphate is so very soluble that it has not been isolated before. It can be obtained by passing sulphur dioxide into the most concentrated solution possible, containing sodium nitrite and sodium carbonate in the ratio of two molecules of the former to three of the latter salt, until the new salt begins to crystallise out. It occurs in small, sparkling, short, thick prisms containing $5\text{H}_2\text{O}$ and is exceedingly unstable. It is neutral to litmus. By dissolving the salt in concentrated, faintly alkaline solution of barium chloride, a precipitate is obtained, flocculent at first, but becoming crystalline and dense, of barium or barium sodium nitrilosulphate.

*108. "The Decomposition of Hydrocarbons at High Temperatures." (Preliminary Note). By W. A. BONE and D. S. JERDAN.

For some months past the authors have been studying the decomposition of various hydrocarbons at a temperature of about 1150° . Since methane is the only hydrocarbon produced by the direct combination of carbon and hydrogen at 1200° , it seemed probable that any hydrocarbon would, at this temperature, be decomposed, yielding ultimately carbon, hydrogen, and a small percentage of methane. So far the authors have only studied the decomposition of methane and acetylene in detail, but the recent publication of a paper "Ueber pyrogenetische Reactionen organischer Substanzen" by W. Ipatiew (*Ber.*, 1901, xxxiv., 496), in which he announces his intention to investigate the decomposition of hydrocarbons at high temperatures, makes it desirable that they should publish this note.

The method adopted by the authors, which will be described in detail in a future communication, consists in admitting the pure hydrocarbon into a vacuum, glazed porcelain tube (length 60 c.m., internal diameter 12 m.m., capacity about 65 c.c.), nearly the whole length of which has been previously heated to about 1150° in a specially designed Fletcher furnace. The experimental tube is properly jacketed so as to prevent any diffusion of furnace gases into it. The temperature, which can be maintained practically constant for several hours, was ascertained by means of a Roberts-Austen electrical pyrometer. After the gas under investigation has been subjected to the high temperature for a definite time, it is quickly pumped out into tubes over mercury.

Acetylene is very rapidly decomposed at 1150° ; after

one minute not more than 10 per cent, and after five minutes only a mere trace of it remains. Considerable quantities of a saturated hydrocarbon, which subsequent examination has shown to be methane, are formed during the early stages of the decomposition, and afterwards this methane is slowly, though never completely, resolved into its elements. Neither benzene nor ethylene are formed at any stage of the decomposition, and, after the final disappearance of acetylene, the gaseous products contain hydrogen and methane only. Carbon is liberated during the early stages as "lamp-black," which doubtless arises from the rapid decomposition of the acetylene, but afterwards it is only deposited on the inner surface of the tube in a form much resembling "gas carbon."

The following figures show the percentage composition of the gases obtained in a series of experiments in which the time of heating varied from 1 minute to 3 hours:—

Time	1 min.	5 mins.	15 mins.	1½ hrs.	3 hrs.
Acetylene ..	10.0	trace	nil	nil	nil
Methane ..	16.0	21.5	16.0	7.75	3.0
Hydrogen ..	74.0	88.5	84.0	92.25	97.0

Methane is resolved into its elements at 1150° more rapidly than would be generally supposed. The decomposition, however, only occurs at the surface of the containing tube, where the carbon is deposited in a form much resembling "gas carbon" in appearance. At no stage of the decomposition was it possible to detect the formation of acetylene, ethylene, or any other unsaturated hydrocarbon. A careful examination of the gas left after 15 minutes' heating has shown that it contains no other saturated hydrocarbon than methane. The following figures indicate the percentage composition of the gas obtained at the end of 5, 15, and 30 minutes respectively, leaving out of the reckoning any small amount of nitrogen it contained:—

Time	5	15	30 minutes
Methane	37.5	12.25	6.6
Hydrogen	62.5	87.75	93.4

The authors are now completing a series of experiments on ethane, and then propose to extend the research to other typical hydrocarbons, and to temperatures other than 1150° .

*109. "Note on the Sugars from Cellulose." By HENRY J. H. FENTON.

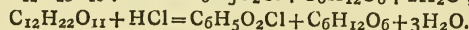
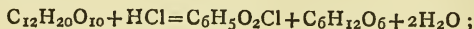
In several previous communications (Fenton and Gostling, *Trans.*, 1898, lxxiii., 554; 1899, lxxv., 423; 1901, lxxix., 361, 807), it has been shown that various forms of "cellulose" (such as filter-paper and cotton) give considerable yields of the chloro- or bromo-derivatives of methylfurfural when they are heated with dry hydrogen chloride or bromide dissolved in an appropriate solvent. It was further shown that the formation of the bromo-derivative in any notable quantity is indicative of the presence of a *keto*hexose nucleus or grouping, and the existence of one or more such groupings in "cellulose" was consequently inferred. Recent experiments indicate that the same observations apply also to the *chloro*-derivative.

After treatment of cellulose in this manner with dry hydrogen chloride and complete removal of the methylfurfural derivative by washing repeatedly with ether, a dark brown residue is left which, in the case of filter-paper, still shows a fibrous structure, and amounts to about 90 per cent of the material taken. If this residue is digested with warm water, a solution is obtained which gives all the reactions of *dextrose*. It is strongly dextro-rotatory, and with phenylhydrazine acetate, on heating, yields *glucosazone* (m. p. $204-206^{\circ}$, $N=15.83$, theory requiring 15.64 per cent). On evaporating the solution to small bulk in a vacuum, and adding alcohol, a syrup is at once precipitated, which solidifies on standing, and the solution continues to deposit crystalline crusts after a time. Mannose appears to be excluded from the fact that phenylhydrazine gives no precipitate in the cold even after standing for several hours.

Fifty grms. of Swedish filter-paper were treated in the manner above described, the solvent used being carbon tetrachloride, and the resulting chloromethylfurfural estimated by weighing the crystals. The residue was then extracted with water, and the dextrose estimated by means of Fehling's solution. The results gave chloromethylfurfural 3.1 grms., and dextrose 1.57 grms. At first sight therefore it would appear that the methylfurfural derivative is produced in excess. But it is found that when dextrose is treated in the same manner, a considerable portion is destroyed, leaving a black residue. A blank experiment was made with 5 grms. of dextrose under exactly similar conditions, with the result that the carbon tetrachloride extract weighed only 0.01 grm., and the residual sugar 2.2 grms. If it be assumed that the dextrose resulting from the action on cellulose is destroyed to a similar extent, the calculated amount of this sugar produced in the first experiment mentioned would be 3.54 grms. This, it will be seen, is approximately the quantity required (3.86 grms.) on the assumption that the chloromethylfurfural and dextrose are produced in *equal molecular proportions* (144.5 : 180).

These facts appear to be of especial interest in relation to the recent work of Skraup and König (*Ber.*, 1901, xxxiv., 1115), in which it is stated that the cellulose acetate obtained by the action of acetic anhydride and concentrated sulphuric acid on filter-paper is an *octoacetyl biase*, and that this on hydrolysis yields "cellose," $C_{12}H_{22}O_{11}$.

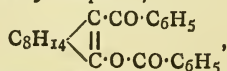
A simple explanation of the results above mentioned would be afforded if it be assumed that this "cellose" (and its antecedent) contains both ketohexose and aldohexose residues, so that the action of hydrogen chloride could be represented by one of the following equations:—



If the brown residue which remains after extracting the chloromethylfurfural and sugar be dried, and again treated with dry hydrogen chloride as before, a further yield of both products is obtained, and experiments are being made to ascertain to what extent this treatment may be repeated, and what is the nature of the final residue.

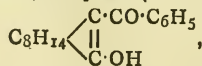
*110. "Studies in the Camphane Series." Part IV. By M. O. FORSTER.

1-Benzoxyl-2-benzoylcamphene,—



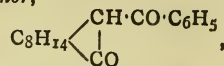
prepared by the action of benzoyl chloride on the sodium derivative of camphor dissolved in toluene, crystallises from alcohol in colourless, highly refractive prisms, and melts at 144°; a 4 per cent solution in chloroform has the specific rotation $[\alpha]_D = +189.7^\circ$.

1-Hydroxy-2-benzoylcamphene (enolic α -benzoylcamphor),



obtained by hydrolysing the foregoing substance with alcoholic potash, crystallises from alcohol in flattened octahedra, and melts at 89°; a 2 per cent solution in chloroform gave $[\alpha]_D = +281.1^\circ$. It dissolves in sodium carbonate, and an alcoholic solution develops immediately an intense purple colouration with ferric chloride; cold concentrated sulphuric acid and boiling formic acid convert it into the ketonic modification, a change which also proceeds spontaneously when the substance is dissolved in organic media, the transformation into the ketone being accelerated by addition of piperidine or by exposure to sunlight. The sodium, copper, and ferric derivatives are crystalline, and are freely soluble in organic liquids; the phenylurethane derivative melts at 117°, and the acetyl derivative, which crystallises from alcohol in lustrous, rectangular plates, melts at 107°.

α -Benzoylcamphor,—



produced on boiling a solution of the isomeride in formic acid, crystallises from alcohol in colourless, transparent prisms melting at 87–88°; a 2 per cent solution in chloroform gave $[\alpha]_D = +125.0^\circ$. The alcoholic solution remains indifferent to ferric chloride at first, but a green colour is rapidly developed, and changes ultimately to bluish-violet. Fusion converts the ketone into the enolic isomeride, and the specific rotation of a solution in chloroform gradually increases until $[\alpha]_D = +216^\circ$, the value to which the optical activity of the enol diminishes.

*111. "On the Decomposition of Carbon Dioxide, when submitted to Electric Discharge at Low Pressures." By J. N. COLLIE, Ph.D.

During some experiments that were being made on the relative resistance of carbon dioxide in a vacuum tube to the electric spark from an induction coil, it was noticed that the resistance varied considerably. At the same time, the colour of the incandescent gases at the negative electrode was seen to change. In order to ascertain what changes had taken place in the composition of the gas after sparking, the contents of the vacuum tube were pumped out, and analysed. It was found that considerable decomposition had occurred into carbon monoxide and oxygen, $2CO_2 = 2CO + O_2$. A series of experiments gave the following results:—When carbon dioxide at 5 m.m. pressure is sparked in an ordinary vacuum tube for ten minutes, 63 per cent of the gas is decomposed, and when sparked for 5, 3, 2½, 1, and even ½ a minute, as much as 58–60 per cent decomposition occurs. In fifteen seconds one experiment showed that 48 per cent was decomposed, whilst in some others when the gas was sparked for ten seconds at 10, 3, and 1 m.m. pressure, 32, 55, and 65 per cent respectively was decomposed. Most of these experiments were made with platinum electrodes. Aluminium electrodes gave a rather higher amount of decomposition, whilst with an electrodeless tube only 50 per cent suffered decomposition after one minute sparking.

Another interesting observation was that if the platinum electrodes are allowed to become red-hot, re-combination at once occurs between the carbon monoxide and oxygen till the gas which remains, instead of containing the products of decomposition of 60 to 70 per cent of the carbon dioxide, is almost pure carbon dioxide.

Under electrical strain, therefore, at low pressures, carbon dioxide is a very unstable gas, but when the products of decomposition come in contact with red-hot platinum wire re-combination occurs. Carbon monoxide, even after twenty minutes' sparking, seemed almost unchanged, and gave only a faint turbidity with baryta water. When a mixture of carbon dioxide and hydrogen is sparked at reduced pressures small quantities of a gas, which seems to be methane, are formed, but under no conditions could formaldehyde be detected. It is probable that the methane is formed by the action of hydrogen on carbon monoxide.

*112. "Halogen Derivatives of *p*-Cymene from Substituted Nitro-Camphanes." By M. O. FORSTER and W. ROBERTSON.

The oil which accompanies the conversion of 1:1-bromonitrocamphane into the anhydride has been identified as bromo-*p*-cymene $[CH_3 : Br : C_3H_7] = 1 : 2 : 4$.

The anhydride of 1:1-chloronitrocamphane, prepared by dissolving that substance in cold concentrated sulphuric acid, crystallises from alcohol in colourless opaque prisms, and melts at about 230°; chloro-*p*-cymene is formed during the production of this compound. The isomeride, $C_{10}H_{14}ONCl$, obtained by the action of an alcoholic solution of hydrochloric acid, crystallises in transparent, six-sided plates, and melts at 248°; it forms a benzoyl derivative, which melts at 166°.

The *hydroxylamino*-derivative, $C_{10}H_{17}O_2N_2Cl$, prepared from either compound by the action of alcoholic hydroxylamine, melts at 187° ; the *benzoyl* compound melts at 164° .

The *nitro*-derivative of the anhydride melting at 248° crystallises in flat prisms, which melt at $71-72^\circ$; reduction with zinc and acetic acid regenerates the anhydride.

113. "On a Theory of Chemical Combination." By G. MARTIN.

Atoms are complex structures analogous to a benzene nucleus which in their ordinary state are incapable of acting on each other, but if by some cause the atomic ring is broken, the atoms become capable of acting together. In this state they are said to be "ionised." Chemical action will only take place of its own accord when the rate of variation of ether strain experienced by a molecule, produced by the approach and recedence of neighbouring molecules, is of such a rate as to coincide with an internal rate of vibration of an atom or molecule. The atoms thus become ionised. The dissociation of gaseous molecules is controlled by two circumstances:—

a) The gradual increase of temperature, by increasing the velocity of the atoms in the molecule, may cause it to decompose of its own accord; (b) if the rate of vibration of ether strain happens to coincide with the rate of vibration of the molecule, the dissociation will occur long before cause (a) of itself would cause decomposition.

In dissociation the atoms need not necessarily be ionised. The rapid increase of velocity of reaction with the temperature is due to the coincidence of the time rates of atomic vibration, and the rate of variation of ether strain.

If two gaseous molecules, A and B, act on each other at (say) t° , then the same reaction will also take place at higher temperatures— t'° and t''° —the condition being that at t° the rate of variation of ether strain is approximately equal in value to the rate of vibration of the atoms of the molecule. But at t'° and t''° the rate of variation of ether strain is respectively double or treble the rate of atomic vibration. It may happen, however, that the products of the change are incapable of existing at these temperatures. The atoms will, however be ionised at each of the ranges t° , t'° , and t''° , no matter whether any reaction takes place or not. At intermediate temperatures no reaction will take place. In certain cases we have experimental evidence of such ranges of temperature, silicon hexachloride, Si_2Cl_6 , for example, is stable enough at the ordinary temperature, but above 300° its vapour begins to dissociate, and at 800° it is entirely decomposed. If, however, the temperature be raised rapidly above 1000° no decomposition of the substance occurs. The substance, therefore, is stable above 1000° and below 350° , but will not exist at intermediate temperatures.

The occurrence of these temperature ranges may be obscured by the fact that the products of the reaction may exist continuously from one range to the other.

A reaction will only proceed to completion when the rate of variation of ether strain necessary to cause the molecules to react together does not also induce the products of the change to decompose. Complete reactions occur only very seldom, as a complex molecule has so many modes of vibration that it is not difficult for it to be affected at almost any temperature.

114. "On the Occurrence of Paraffins in the Leaf of Tobacco." By T. E. THORPE, C.B., F.R.S., and J. HOLMES.

In connection with the working of the Revenue Act, which imposes a limit upon the amount of oil which may be present in manufactured tobacco, the authors have had occasion to study the nature of the material which is extracted from tobacco by "petroleum-ether." In the extract thus obtained, they have discovered the presence of two paraffins, *hentriacontane*, $C_{31}H_{64}$, melting at $67.8-68.5^\circ$, and *heptacosane*, $C_{27}H_{56}$, melting at $59.3-59.8^\circ$, which are present in the leaf in about equal amounts to

the extent, in the aggregate, of rather more than 1 part per 1000.

In Kentucky and Virginia leaf, the mixed hydrocarbons, in three separate preparations, had the following melting-points:—Western leaf, $63.0-63.8^\circ$; "wrappers," $63.5-64.0^\circ$; "fillers," $63.7-65.0^\circ$. The authors are of opinion that the snow-white substance of satiny lustre extracted from Kentucky tobacco by Kissling (*Ber.*, 1883, xvi., 2432), which he found to melt at 63.0° , and which he regarded as probably an impure mellissyl mellisate, and the substance of similar appearance found by him among the constituents of tobacco-smoke, melting at 64.5° , but which he regarded as a hydrocarbon, are in reality the same products, and identical with the mixture of the two paraffins, the heptacosane, $C_{27}H_{56}$, and hentriacontane, $C_{31}H_{64}$, of Krafft, which the authors have found to be present in all the American tobaccos examined by them.

115. "Two New Substances in Lemon Oil." By H. E. BURGESS.

If 3 or 4 litres of the terpenes obtained during the distillation of the lemon oil are well shaken with a cold solution of sodium metabisulphite, a small quantity of a crystalline compound is formed which can be separated and washed with alcohol and ether. This on being decomposed in the usual way gives an aldehyde of which the constants are very different from those of citral:—Boiling-point, $80-85^\circ$ at 15 m.m.; optical rotation, $+0.30^\circ$; refractive index, 1.4314 at 20° .

It has an odour resembling cocoanut oil. On shaking the aldehyde with hydrogen peroxide and caustic soda solution it is at once polymerised into a solid form which can be re-crystallised from alcohol.

It forms an oxime melting at 35° , and on oxidation with potassium permanganate it gives an oily acid; from the ammonium salt the silver, copper, and magnesium salts have been prepared and analysed.

Apparently the same aldehyde exists in orange oil, but was not found in the terpenes as in the case of lemon oil.

A crystalline substance was obtained by shaking together 1 litre each of acetone and lemon oil, and then adding about 200 c.c. of water, when it separates into two layers; the lower portion was separated, and allowed to stand for twenty-four hours, when small crystals were formed in the globules of oil floating on the surface; these were filtered off, and re-crystallised from alcohol and ether.

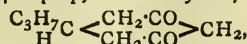
Several such separations may be made from each quantity of oil, but the total yield from 1 litre was extremely small. The crystals so obtained melted at 145° . They are sparingly soluble in alcohol, the solution having a marked blue fluorescence.

Several combustions have been made of the re-crystallised substance which forms a crystalline dibromide, and is oxidised to oxalic acid and carbonic acid.

116. "Preparation and Properties of 2:6-Diketo-4-isopropylhexamethylene (2:6-Dihydroxy-4-isopropyl-dihydroresorcinol)." By A. W. CROSSLEY.

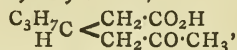
Ethyl 2:6-diketo-4-isopropylhexamethylene-3-carboxylate, obtained by the condensation of isobutylideneacetone and ethyl malonate, separates from a mixture of benzene and light petroleum in small needles melting at 101° . When boiled with sodium carbonate or potassium hydroxide solution it yields:—

2:6-Diketo-4-isopropylhexamethylene,—



which crystallises from dilute alcohol, with $1H_2O$, in well formed needles, melting at 67.5° . Its constitution is proved by its method of formation, and because on oxidation with sodium hypobromite it yields β -isopropylglutaric acid. The silver salt is an insoluble white precipitate, and the dioxime separates from dilute methyl alcohol in clusters of stumpy needles, melting somewhat indefinitely about 145° .

When hydrolysed with barium hydroxide diketoisopropylhexamethylene is converted quantitatively into *β*-isopropyl-γ-acetylbutyric acid,—



which is an almost colourless oil, boiling at 195° (39 m.m.).

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 28th, 1901.

Prof. EVERETT, Vice-President, in the Chair.

THIS meeting, by invitation of Prof. W. G. Adams, was held in the Wheatstone Laboratory, King's College.

A paper on "*The Effect of a High Frequency Oscillatory Field on Electrical Resistance*" was read by Mr. S. A. F. WHITE.

The object of this paper is to discover if the action of light upon the electrical resistance of selenium can be imitated by using high frequency electrical oscillations. It is found that such oscillations permanently increase the resistance of selenium. The effect of a rise of temperature is to increase the resistance of a piece of low resistance, and decrease the resistance of a piece of high resistance. The effects of the field on a piece of high resistance can be reversed by exposure to light or by re-heating and subsequent cooling. In the case of tellurium a high frequency field temporarily decreases the resistance, as also does a rise in temperature. Repeated heating and cooling of a piece of tellurium permanently increases its resistance. It seems probable that all of the effects are due to rise of temperature caused by minute sparks within the mass. The rise in resistance by alternate heating and cooling may be due to the formation of tellurides with the metal of the electrodes. The large negative temperature effect of tellurium suggests that it might be usefully employed in the detection of heat radiation.

The CHAIRMAN expressed his interest in the paper, and drew attention to the very rapid action of light upon selenium.

Prof. ADAMS said that as the effects here noticed were not so rapid as in the case of light they were probably due to change in temperature.

Prof. BOSE said he had tried the effect of Hertzian radiation upon thin layers of various metals, and found an increase of resistance in the case of selenium and a decrease in the case of tellurium. The effect of radiation is confined to a few layers on the surface of the conductor, but it appears that it is of the same nature in continuous solids as in coherers.

A paper by Mr. E. C. C. BALY and Dr. H. W. SYERS, on "*The Spectrum of Cyanogen*," was read by Mr. BALY.

The authors have been able to obtain the spectrum of cyanogen by allowing the pure gas to flow through a vacuum tube, and observing from the end of the tube. This is necessary on account of the brown deposit of paracyanogen which renders observation in the ordinary way impossible. The spectrum obtained differs from the flame spectrum, and consists of a series of equidistant flutings through the whole of the red and yellow—some-what recalling those of the positive band spectrum of nitrogen. The experiments prove that (1) the Swan spectrum is not produced by a carbon compound which does not contain oxygen; (2) the Swan spectrum is that of an oxide of carbon, as it is only produced by carbon monoxide; and as this spectrum is changed at once into the carbon oxide spectrum by admission of oxygen or by intense electric discharge; and further, as the carbon oxide spectrum is invariably given by carbon dioxide there can be no doubt that (3) the Swan spectrum is that of carbon monoxide, and the carbon oxide spectrum that of carbon dioxide.

Mr. GASTER said that this paper might throw light on the discussion of the arc where cyanogen, carbon monoxide, and carbon dioxide are present. The presence of cyanogen might be able to explain the hissing of the arc.

The Society then adjourned until next October.

CORRESPONDENCE.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

SIR,—However original Mr. Bennett Blackler's process may be, and however accurate it may be in the case of pure ammoniacal salts—which, knowing beforehand that they are pure, there is no necessity to analyse—it must of necessity fail in the case of a complete analysis of commercial sulphate of ammonia, such, for instance, as put in the market by the London and provincial gas companies, or in a mixture of superphosphate of lime and sulphate of ammonia, to say nothing of acid and basic phosphates of ammonia and mixtures thereof.

Let Mr. Blackler estimate in a commercial sample of sulphate the *free acid*, the moisture, the insoluble, the ammonia as determined by this method, and the total sulphuric acid, together with the nitrogen existing in other combinations than sulphate, and see whether, even after making allowance for free acid, his figures do not total considerably over 100.

The complete analysis of commercial sulphate is not done by a magic wand process. Let Mr. Blackler fill up the following blank form from his results after having made the corresponding determinations on an actual commercial sample:—

	Per cent.
Moisture	—
Free sulphuric acid	—
Combined sulphuric acid	—
Ammonia as determined by Mr. Blackler's process:—	
1. (NH ₃) equivalent to combined sulphuric acid	—
2. Excess of ammonia over that required to saturate combined H ₂ SO ₄ after deducting the excess of ammonia due to free acid and which in his process is estimated as sulphate of ammonia ..	—
Insoluble organic matter	—
Insoluble inorganic matter	—

Again, unless an ash determination were made, it would be quite possible to fake up sulphate, &c., of ammonia most grossly with acid sulphate of soda if this process were relied on solely.—I am, &c.,

J. G. McINTOSH.

AMERICAN v. ENGLISH SPELLING.

To the Editor of the Chemical News.

SIR,—The recent correspondence in the CHEMICAL NEWS anent American v. English spelling of chemical terms impels me to give a brief history of the "rules" which have been several times referred to.

In view of the variable usage in the pronunciation, and to a lesser extent in the spelling, of chemical terms, the Chemical Section of the American Association for the Advancement of Science appointed a committee at the New York meeting in 1887 to take the subject under consideration. This committee consisted of Prof. Thomas H. Norton, of the University of Cincinnati, Dr. H. Carrington Bolton, of Washington, and Prof. Edward Hart, of Lafayette College. An informal report was made

at the Cleveland meeting the next year, and the committee was continued; at that time I was added to the committee, and acted as its secretary.

In May, 1889, quite a long list of words, the spelling or pronunciation of which might be considered doubtful, was widely distributed among American chemists. Based on the replies received, a report was made to the section at the Toronto meeting, and fully discussed. At that meeting the committee of the Section was made a special committee of the Association. The report of this year was printed and distributed with requests for criticism. The third report of the committee was read and discussed at the Indianapolis meeting in 1890. On a large proportion of the words substantial agreement had been reached, and a list of the remainder was for the third time sent out. The fourth and final report of the committee was adopted by the Chemical Section at the Washington meeting in 1891, and afterwards by the Association. It was also reprinted in chart form by the Bureau of Education, and distributed to secondary schools all over the country. The printed reports and references to the committee will be found in the *Proceedings* of the Association as follows:—1888, p. 131; 1889, pp. 186—194, 478; 1890, pp. 150—158; 1891, pp. 173—178; 1893, p. 366.

The fact that there was great divergence in usage in this country seemed to call for the appointment of such a committee; the sole aim of the committee was to secure if possible a uniform usage; to this end the co-operation of chemists generally was sought. The original list and the three successive reports were sent to every American chemist whose address could be secured, with urgent requests for full comment and criticism. Several attempts were also made to secure the co-operation of English chemists, but I think I am not in error in stating that no notice was taken of these requests. It may be added that every doubtful point was submitted not only to chemists, but to a number of philologists.

That the work of this committee has not been successful in harmonising even American usage must be admitted. Many writers follow the recommendations of the final report; more do not. Those who have criticised the final report most freely are those who refused all co-operation while the work of the committee was in progress.

Perhaps I may add that in only two instances did the Chemical Section reverse the views of the committee. The committee favoured "sulphur," even though as high an authority as Professor March considered "sulfur" to be correct, and a majority of the committee favoured "aluminium" rather than "aluminum," but commercial usage had so popularised the latter form that the committee was reversed.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University,
Lexington, Va., June 7, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

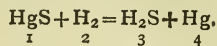
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxii., No. 23, June 10, 1901.

Neutralisation. Titration of Acids and Alkalis of Complex Function.—M. Berthelot.—Complex functions of acids and alkalis can be detected, and even estimated to a certain extent, by various colouring-matters. The number of indicators apt to vary under the action of acids or alkalis being considerable, and the amount of divergence varying for each one, according to the conditions of equilibrium which determine the functions of the acids or alkalis producing the divergence, the author limits him-

self to the indicators tournesol, methyl-orange, and phenolphthalein. With these he experiments on acid-alkalis derived from the acid alcohol, e.g., glycolic, &c., the three oxybenzamic acid isomers, and hippuric acid, the normal amido-derivative of oxyacetamine and benzoic acid.

Experimental Verification of a Law of Mechanical Chemistry.—H. Pélabon.—The action of hydrogen on mercury sulphide, and the inverse reaction of sulphuretted hydrogen gas on mercury, leads to the investigation of a system containing four volatile bodies,—



Using the indices 1, 2, 3, 4 respectively for the four bodies, it is easily seen that the general relation existing between the partial pressures of the gases and vapours contained in the system is of the form—

$$\log \frac{p_1^{2v} p_2^{2v}}{p_3^{2v} p_4^{2v}} = F(T);$$

$2v$ is the volume occupied by all the molecules of the simple and compound bodies. If any of the pressures become zero, the expression is simplified into—

$$\frac{p_1 p_2}{p_3 p_4} = f(T).$$

The author submits this formula to an experimental verification.

Action of a Metallic Hydrate on Solutions of Salts of other Metals. Basic Salts containing Two Metals.

—A. Recoura.—The author's experiments verify those results already published on the action of metallic chlorides, and show that in reactions in which 4CuO plays a part, and which reappear so frequently in the history of the copper compounds. He has compared them together in the form of a table, giving in each case the quantities of the various sulphates which combine with 4CuO . The compounds not being crystalline, the water of combination was not determined. In all cases it was found that cupric hydrate combines with the same quantity of all the sulphates examined, with the exception of nickel, to give the compound $3\text{CuO}(\text{MOSO}_3)$, corresponding to the sulphate, $3\text{CuO}(\text{CuOSO}_3)$; the latter substance being formed when hydrate of copper comes in contact with a solution of copper sulphate.

The Imidodithiocarbonic Ethers, $\text{RN}=\text{C}(\text{SR}')_2$.—Marcel Delépine.—The author's experiments on the imidodithiocarbonic ethers give results confirming the formulæ and reactions previously admitted. The details of analysis on which they are based were published at the same time as the individual investigation of the ether in question. Thanks to the new method of preparation, in which the yield is considerable, the author hopes to be able to continue his research and extend it to the derivatives of the thiosulphocarbamates of the secondary amines, which substances react very easily on the alcoholic iodides, and in a similar manner to that which he discovered with regard to several fatty amines and piperidine.

Active Erythrites.—L. Maquenne and G. Bertrand.—In two previous papers, the authors announced the existence of two active tetrites, predicted by theory, and described their principal characteristics. These two substances, called *l*-erythrite and *d*-erythrite, are now studied more carefully, and, having completed their chemical history, all previous predicted properties were verified. The results also show that these two substances represent the optical antipodes of active erythrite; that which is formed during the hydrogenation of erythrose corresponding to ordinary tartaric acid, whilst the other corresponds to *l*ævo-tartaric acid, and, in consequence, ought to have a place by the side of this in the left series.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., No. 3.

Action of Hydrogen on Protosulphide of Bismuth.

—H. Pélabon.—Already noticed.

The Double Chlorides of Uranyl and the Alkaline Metals; and the Hydrochlorate of Chloride of Uranyl.
—J. Aloy.—Already inserted in full.

On Oxide of Bismuth.—P. Thibault.—Already inserted in full.

Specific Molecular Heat of Dissociable Gaseous Compounds.—M. Ponsot.—Already noticed.

The Complex Salts of Platinum. (IV.). Alkalino-earth Oxalonnitrites.—M. Vèzes.—Already inserted in full.

The Dialcylamido-ortho-benzoylbenzoic Acids and their Derivatives.—A. Haller and A. Guyot.—Following on their previous researches on the preparation of these acids, the authors have now examined the preparation and properties of some of their derivatives. The dialcylparamido-orthobenzoylbenzoic acids are obtained by the condensation of equal molecules of phthalic anhydride and a tertiary aniline of which the para-position is not occupied. For this reaction to take place, it is, as a rule, necessary to use a condensation agent, such as AlCl_3 . Dimethylamidobenzoylbenzoic acid is easily obtained in the pure state, with a return of 75 per cent of theory, by the condensation of phthalic anhydride and dimethylaniline in the presence of chloride of aluminium. It occurs in bright yellow prisms, fusible at about $202-203^\circ$, having a very sweet taste and almost insoluble in water, ether, benzene, toluene, and chloroform, but very soluble in hot methylic and ethylic alcohol, from which they crystallise on cooling with or without a molecule of alcohol of crystallisation. Diethylamidobenzoylbenzoic acid is prepared in exactly the same manner as its lower homologue, but replacing the dimethylaniline by diethylaniline. It has analogous properties, it fuses at 180° , and is very sweet to the taste. Ethylbenzylamidobenzoylbenzoic acid is obtained in a similar manner to its lower homologues by the condensation of ethylbenzylaniline with phthalic anhydride in the presence of chloride of aluminium. The detailed preparation of this acid is given, as it differs in some important particulars from that of the others.

No. 4.

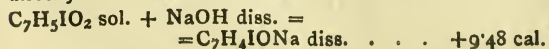
The Blue Oxide of Molybdenum.—Marcel Guichard.—Already noticed.

The Action of Water on Pentachloride of Molybdenum.—Marcel Guichard.—Already inserted in full.

Action of Bromide of Aluminium on some Acyclic Chlorised Hydrocarbons.—Ch. Pouret.—By the action of powdered aluminium on the perchlorised derivatives CCl_4 , C_2Cl_4 , and C_2Cl_6 in the presence of bromine, the author has in every case obtained hexabromomethane, C_2Br_6 , and at the same time some resins. He now fully describes the preparation of bromoform, bromide of methylene, and bromide of methyl.

Thermic Data relative to Orthomonochlorobenzoic Acid.—G. Massol.—The heat of formation of the ammoniacal salt has been found to be lower than that of benzoate of ammonia. Again, the heat of formation of the potash salt with half a molecule of water was found to be equal to that of benzoate of potash, but it is evident that the anhydrous salt would give off a slightly greater amount of heat. Orthomonochlorobenzoate of soda gave a heat of formation higher than that of the benzoate of soda.

Thermic Data relative to Orthomoniodobenzoic Acid.—G. Massol.—This acid is too slightly soluble in water to allow of its heat of solution being determined directly. Its heat of neutralisation is—



The anhydrous salt was obtained after prolonged desiccation at 120° ; its heat of solution in water is $+2.96 \text{ cal.}$ at 12°C. for 1 molecule (molecular weight = 270) in 4 litres.

The Cyclic β -Diketones.—Georges Leser.—Already noticed.

Preparation and Properties of Dialcylamido-anthraquinones.—A. Haller and A. Guyot.—A long paper, not suitable for useful abstraction.

On some New Colouring-matters.—E. Grimaux and Leon Lefèvre.—Colours derived from triphenylmethane and its homologues are dinitrated and then acted upon, according to the known methods, by phenols, naphthols, or amines. In this manner, triamines, diamines, or monoamines were operated upon, and new colours produced.

Blue Colouring Materials derived from Triphenylmethane.—E. Grimaux.

Rose Colouring Materials derived from Triphenylmethane.—E. Grimaux.

Derivatives of Triphenylmethane.—E. Grimaux.

Preparation of Alkylised Meta-amino-phenols.—E. Grimaux.

The Colouring Materials derived from the Alkylised Meta-amino-phenol Ethers.—E. Grimaux.—The above five papers all briefly describe the author's experiments and the preparation and properties of the materials referred to.

The presence of Oxysulphocarbonate of Iron in the Waters of the Rhone.—H. Causse.—Already noticed.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., His Grace the Duke of Northumberland, K.G., President, in the Chair. Mr. A. C. Allen was elected a Member.

Institute of Chemistry of Great Britain and Ireland.—*The Final Examination for the Associateship in the Branch of Biological Chemistry.*—An Examination in this Branch will be held at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., in October next. The exact date will be communicated to intending candidates. Candidates desirous of presenting themselves are required to notify the Registrar on or before Tuesday, the 3rd day of September, 1901. The Examination is open to any candidate whose application for admission to the Final Examination has been accepted by the Council, and any candidate who has passed the Intermediate Examination of the Institute. The Examination will extend over at least four days, and may be theoretical, practical, written, and oral, and the syllabus will include the following:—Biological Chemistry, with special reference to the chemistry and bacteriology of foods, water, sewage, and effluents, and the practical applications of Biological Chemistry to industries. Examinations in the branch of Biological Chemistry of the Final Examination will be held annually in October, while the Examinations in the other branches will be held in January and July as heretofore. Candidates intending to enter for the Final Examination in the branch of Biological Chemistry are recommended to take (after passing the Intermediate Examination, or any examination qualifying for admission to the Final) a course of study covering the following work:—A course of 40 to 50 lectures on the Morphology and Physiology of Micro-organisms. Practical work to include—(a) Microscopy, the preparation, staining, mounting, drawing, and recognition of specimens; (b) the preparation and study of pure cultures; (c) the conduct of fermentation experiments and the study of chemical changes brought about by bacteria, moulds, yeast, &c.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2172.

A NEW TEST FOR CHLORINE FOR USE WITH THE BLOWPIPE.

By HENRY W. NICHOLS.

A PIECE of absorbent paper moistened with a solution of cobalt chloride turns blue when warmed.

A piece of absorbent paper moistened with a solution of cobalt bromide or iodide turns green when warmed.

A piece of absorbent paper moistened with a solution of cobalt nitrate turns a deeper rose colour and darkens when warmed.

Paper moistened with solutions of other cobalt salts, when dried in the air, does not turn either green or blue at a temperature below that of the carbonisation of the paper.

Paper moistened with a solution of cobalt nitrate and a soluble chloride acts upon warming as if it were moistened with cobalt chloride.

Upon these facts is based the following tests for chlorine and for the distinction between chlorine and bromine or iodine. This test calls for such apparatus and reagents only as are commonly used in blowpipe work:—

Powder the assay with from one to four volumes of potassium bisulphate. Place the mixture in a closed tube. Moisten a fragment of filter-paper with cobalt nitrate solution and place it in the mouth of the tube. Upon fusing the mixture, the paper under the influence of the hydrochloric acid and sulphuric anhydride given off will turn a bright blue if chlorides are present. If bromides or iodides are present the colour will be green. In case of minute quantities it may be necessary to dry the paper before the colour appears, but ordinarily the sulphuric anhydride evolved by the bisulphate produces the same effect as heating. Although the blue of the cobalt chloride assumes, when faint, a greenish cast, yet it is always distinct from the yellowish-green of bromides. When chlorides and bromides are found together, the paper turns first blue from chlorine and later green from bromine. If but little bromine is present the final colour will be a bluish green. The test is much less delicate for bromides than for chlorides. If but little chlorine is present and much water condenses in the tube, this water may hold back the hydrochloric acid and should be driven into the test paper. When this occurs it is often necessary to heat the paper to bring out the colour, and under these conditions the yellow of the charred paper may produce with the blue a green, somewhat similar to that produced by bromides. Acid potassium sulphate, as purchased, contains too much sulphuric acid and should be fused in platinum until frothing ceases before use; otherwise it froths in the tube in a disagreeable manner. Many bromides contain sufficient chlorine to give a distinct test by this method, a fact that should be remembered when using them for check experiments. The limit of sensitivity of the test has not been determined. The following tests will indicate its suitability for blowpipe work and mineral determinations: two specimens of embolite were tested and both the chlorine and bromine were indicated. A specimen of sodalite (Cl, 7·3 per cent) gave a good reaction for chlorine, as did a specimen of zunyite (Cl, 2·91 per cent) with about 25 per cent of gangue. The white crystalline apatite of Snarum, Norway, gave a good reaction, while a specimen of the green massive Canadian apatite gave no reaction for the traces (0–0·5 per cent) it generally carries.

Chlorides in solution may be tested by dipping a paper into the solution, spreading a drop of cobalt nitrate solu-

tion upon it, drying, and heating. The test thus carried out is not very delicate; moreover, the distinction between chlorides and bromides is obscured, and sulphides and some other substances interfere.

The familiar test for chlorine in the presence of bromine by the generation of chlorochromic anhydride may be advantageously modified for the blowpipe laboratory. In place of the tubulated test-tube a plain test-tube may be used, and in place of the receiver a piece of filter-paper moistened with a saturated solution of sodium carbonate and placed in the mouth of the tube. This alkaline paper retains chromic acid, so that when burned in the forceps the ash will give a chromium reaction with the borax bead. No difficulty will be found in burning the paper while moist, owing to the bromates and chromates present. During the burning the sodium carbonate fuses and collects the ash into a globule which will be a dirty green if it contains much chromium. For the small quantities of material commonly used in mineral testing, a closed tube may be very advantageously substituted for the test-tube whenever the substance tested does not effervesce with acid.—*American Chemical Journal*, xxv., No. 4.

NOTES ON SOME BLOWPIPE TESTS.

By JOSEPH W. RICHARDS.

Closed Tube Test.—This test may easily be made quantitative for approximate determinations of water, volatile sulphur, &c. A weighed amount of material is put into the tube, tapped down, and heated regularly. The upper part of the tube containing the sublimate is then nicked with a file and broken off. If water is being determined, two small corks are put into its ends, to prevent evaporation. The piece of tube and sublimate are then weighed; then the tube is heated until the sublimate is driven off, and weighed again. The results on pyritic ores have proved satisfactory. A piece of göthite gave 10·28 per cent water; theory requires 10·11 per cent. Time, five minutes.

Open Tube Test.—The behaviour of the antimony coat is sometimes different from that usually described in the books. The entirely volatile oxide, Sb_2O_3 , is sometimes the only product, not a trace of the non-volatile Sb_2O_4 being formed. I have observed this in allemontite, dyscrasite, and ullmannite, particularly. It takes nearly a red heat to volatilise this coating, and if the upper end of the tube from which the vapours are escaping be held in the flame, the latter is coloured pale yellowish green (arsenic, pale blue). Penfield is the only writer who mentions the formation of this volatile coating exclusively by some minerals, but his experience as to which give it does not exactly coincide with mine.

It is important when testing in the open tube, if any substance whatever does not give a sublimate in lump, to powder it, and finally to heat with the blowpipe flame from the outside as hot as the glass will stand. Some sulphides, such as sphalerite and argentite, do not roast until thus heated. With these precautions the test is uniformly reliable.

Flame Tests.—When testing for phosphoric acid, the assay on platinum wire is touched when hot to concentrated sulphuric acid, and brought into the outside edge of the Bunsen flame as low down as possible, and as slowly as possible. By thus proceeding, phosphorus can be infallibly detected in any combination, according to my experience, thus rendering unnecessary the ammonium molybdate test. The flame is slightly bluish green close to the wire, greyish green a short distance away, and yellowish green farther off.

When testing similarly for boron, the assay should be held slightly higher, say an inch higher, in a hotter part of the flame. When testing for boron with Turner's mixture, it is an advantage to moisten the mass to a paste

with a drop of concentrated sulphuric acid, and then put moist into the edge of the flame.

Reduction to Metal.—When reducing with soda on charcoal, if an assay proves very refractory, it is uniformly of advantage, and never deleterious, to add some borax to the assay. This is particularly useful in reducing tin oxide, and is to be preferred to potassium cyanide because of its harmlessness.

Test for Fluorine.—The fusion with potassium bisulphate decomposes any fluoride, but the test of the vapours with Brazil wood paper is not reliable. Light, air, and age seem to deteriorate rapidly the sensitiveness of the paper. I have found it more reliable to make the fusion in a rather large closed tube, of say 5 to 8 m.m. diameter, heating regularly with the tube almost horizontal. The silica ring deposits just above the assay, and the odour of the gas is often quite plain. Cool the tube, nick it below the silica ring, break, and hold the upper end vertically under and close to the nose. At this instant the odour of hydrofluoric acid will be perceived with certainty, if any has been driven off, and by a little experience the odour can be distinguished with as much certainty as the smell of ammonia. A still more conclusive proof consists in letting water run slowly over the silica ring. If it is merely a sublimate of a volatile salt, it will be dissolved and disappear; if it is the true silica ring, it will become gelatinous, seen under the lens, and on carefully drying the tube the white ring is again strongly in evidence.

Test for Arsenates.—All give the arsenic odour and coat on charcoal, but sometimes so slowly as easily to escape detection. Mixing with charcoal dust and soda, and fusing in the closed tube or open tube does not invariably give metallic arsenic or the oxide, on account of the heat being insufficient to reduce some arsenates, *e. g.*, of zinc. Putting this mixture in the lower end of an open tube, and playing on it with the reducing flame of the blowpipe directed into the tube, will always give the arsenic coating. All mercury compounds are also thus reduced, and deposit a mercury coating, and it is a good means of testing for antimonates, tellurates, and selenates, while ammonium compounds give ammonia gas.

Test for Silica in the S. Ph. Bead.—Many silicates are attacked rapidly, the bases dissolved, and the silica left either in flocks or as a skeleton. However, on long blowing, some silica dissolves in the bead, and if only a small piece of mineral is used and the blowing is strong, all may dissolve up clear. Hirschwald determined that the bead can dissolve 2.5 per cent of its weight of silica; my tests have shown close to 2 per cent, but that more can be dissolved if other bases are present. For instance, the bead dissolves—

Per cent of silica.

2.25	if no other base is present,			
2.25	3.85	per cent of alumina is present,		
3.03	8.52	"	"	lime
3.40	3.17	"	"	"
4.04	10.91	"	"	zinc oxide is present.

It results from this behaviour, that in silicates rich in bases, an amount of mineral equal to even 30 per cent of the weight of the bead (as in thaumasite) may be dissolved up clear. Two observations will obviate this difficulty. If the mineral is not white, as it is attacked, the edges will become white and clear as it is being dissolved, and the presence of silica thus proved. If the piece is white or clear, the blowing must be interrupted several times, and then with the lens the silica can be recognised floating in the bead. If the bead is clear, a further addition of a lump, say one-third the size of the bead, will always, on further blowing, cause the opalescent milkiness due to silica. By attending to these points, I think that silica can be found with certainty in all these silicates which are easily decomposed.

A different case is presented by those silicates which are attacked slowly and dissolve *en masse*, without showing a skeleton. They are not numerous, and are principally

the silicates of aluminium, glucinum, or zirconium. In such cases, by long blowing (five minutes), enough silica is usually dissolved in a small bead to make it milky opalescent, which silica alone produces when present in such a small amount as even less than three per cent. The presence of silica can thus be proved. The minerals which dissolve slowly in salt of phosphorus and do not contain silica are principally corundum, diaspore, chrysoberyl, cassiterite, spinel, chromite, gahnite, and xenotime. They should be brought to mind and kept in consideration in connection with such few silicates as dissolve very slowly like the above.—*Journal of the American Chemical Society*, xxiii., No. 4.

ON TRIPHENYLCHLORMETHANE.

By M. GOMBERG.

THE recent publication by Norris and Sanders (*Am. Chem. Journ.*, xxv., 54) on the same subject induces me to make a few remarks at this time. It is far from my intention to enter into any controversy whatever. I merely wish to call attention to the following few points:—

(1) My paper on "Triphenylchlormethane" (*Journ. Am. Chem. Soc.*, xxii., 752) was first presented by me at the Columbus Meeting of the American Association for the Advancement of Science, August, 1899. Norris and Sanders state that they have been at work on this subject for about a year. Hence this subject must have been undertaken by them after my paper was presented. It was, however, entirely natural that they should have overlooked the first mention of my paper, since it was given in the Proceedings (*Proceedings American Association for the Advancement of Science*, 1899, xlviii., 152) only by title.

(2) The difference in procedure between my method and that of Norris and Sanders consists in that the latter used, instead of benzene as a solvent, carbon disulphide—a diluent first introduced by Anschütz (*Ann. Chem. Liebigs*, ccxxxv., 341) for Friedel and Crafts' reaction in general. The application of this solvent in the present instance enabled Norris and Sanders to isolate the important intermediate product, the double salt of aluminium chloride and triphenylchlormethane, which was not obtained by me at all.

(3) Norris and Sanders state (*loc. cit.*, p. 59) that the action of sodium upon triphenylchlormethane is entirely negative, even on two weeks' contact in ether. Only on the addition of brombenzene to the above mixture did a reaction take place. One of the several products was a body free from halogen, yet on analysis the carbon and hydrogen did not add up to 100 per cent. The fact that "this compound resembles closely in melting-point, chemical composition, and solubility" the substance (the peroxide) described by me (*Journ. Am. Chem. Soc.*, xxii., 762) shows that it is an oxygen body. One fails to see, however, how Norris and Sanders "discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene." No evidence is given that they excluded all oxygen-carrying reagents, such as sodium oxide, and that this was not the cause of the formation of that body, or that they worked in an atmosphere free from oxygen, and in this way established the non-formation of that body under these conditions. Furthermore, if the substance is really identical with the peroxide mentioned, it is not the result of the action of sodium upon a mixture of the two halogen compounds, but is formed by action of the atmospheric oxygen upon the unsaturated hydrocarbon (triphenylmethyl) which must have resulted in some way from the action of sodium upon triphenylchlormethane alone. (Experiments show that small quantities of the triphenylmethyl are produced in this way). The reaction must, therefore, be analogous to that described by me for

other metals: silver, zinc, and mercury. Only these three metals, in addition to the unsatisfactory results with sodium, are mentioned in my preliminary paper. Other metals, however, and different solvents, have also been tried and are being studied at present. Norris and Sanders now "propose to investigate the action of sodium on ethereal solutions of triphenylchloromethane of varying concentrations." I regret that having cleared up the difficult part of the problem (the action of metals upon triphenylhalogenmethanes) I am not to have, as it appears from Norris's publication, this field to myself for a while longer. It was stated (*Journ. Am. Chem. Soc.*, xxii., 776) in my preliminary paper that only about two-thirds of the theoretical quantity of the unsaturated hydrocarbon is formed. The nature of the other products is being studied, and I find that this varies according to the metal and solvent employed.—*Journal of the American Chemical Society*, xxiii., No. 2.

ON THE IMPORTANCE OF FORMIC ALDEHYDE AS A PRODUCT OF THE PARTIAL COMBUSTION OF ORGANIC COMPOUNDS.*

By S. P. MULLIKEN, with J. W. BROWN and P. R. FRENCH.

It has been shown elsewhere in the *American Chemical Journal*† by Mulliken and Scudder that formic aldehyde is apparently one of the most common products of the partial combustion of organic compounds by hot copper oxide, and that its appearance in minute traces as a result of such combustions ought never to be accepted as sufficient proof that the substance burned contains a methoxyl group. These conclusions were based entirely on qualitative experiments made incidentally in connection with a study of certain colour tests for methyl alcohol. The present investigation is quantitative in character. Its object is to furnish direct proof that the quantities of formic aldehyde which may be obtained from the oxidation of various typical and purified non-methoxylated compounds are, in general, greater than could arise from accidental impurities in the substances used.

Before proceeding to a description of these experiments, allusion should be made to the few scattering earlier investigations which have a more or less direct bearing on the matter under consideration. Legler (*Ann. Chem. Liebigs*, ccxvii., 382; *Ber. d. Chem. Ges.*, xviii., 3343), claims to have found formic aldehyde in small quantities among the products of the phosphorescent combustion of ethyl ether in presence of metallic platinum. Pratesi (*Gazz. Chim. Ital.*, xiv., 221), obtained it from a decomposition of the vapours of boiling ethyl nitrate induced by a strip of incandescent platinum. Its formation was detected by Schützenberger (*Bull. Soc. Chim.*, xxxi., 482), when ethylene was heated with oxygen to 400°; and by Walkow and by Menshutkin (*Ber. d. Chem. Ges.*, xxxi., 3067), when a mixture of trimethylene and air was passed through a red-hot tube. Its occurrence to the extent of 0.5 per cent in wood smoke, which has lately been noted by Pasqualis (*Centrbl.*, 1897, II., 1012), may also be mentioned, although its appearance in this case is no doubt due merely to a secondary oxidation of the methyl alcohol, which is always formed when wood is subjected to destructive distillation.

In our experiments the oxidations were all made by means of the well-known, simple, and efficient apparatus devised by Loew (*Journ. Prakt. Chem.*, xxxiii., 324; cf.

also Tollens in *Ber. d. Chem. Ges.*, xix., 2135), for the preparation of formic aldehyde from methyl alcohol. Loew early used this apparatus for the partial oxidation of several non-methoxylated substances. Ethyl ether, ethyl acetate, and ethylamine, all gave him acetaldehyde, while toluene yielded some benzaldehyde; but no substance other than methyl alcohol is mentioned as having given formic aldehyde, means for detecting small quantities of formic aldehyde in the presence of much acetic aldehyde being at that time unknown.

In Loew's method a stream of dry air, more or less fully saturated with a combustible vapour, is aspirated through a long tube of infusible glass containing a short coil of oxidised copper gauze, the latter being first brought nearly to redness by the temporary application of a gas flame. The copper oxide of the roll serving as an oxygen carrier, the roll continues to glow brightly, after the gas flame is withdrawn, as long as the combustible mixture is supplied. The liquefiable products of the reaction are condensed by passage through a series of well-cooled bottles containing water, which are interposed between the combustion tube and the suction-pump.

In our work the suction was supplied by a single Richards water aspirator run at nearly its full capacity. The combustion tube was 2 feet long and supported near its lower end by a clamp protected by asbestos. The copper roll, 2 inches in length, was made of fine-meshed gauze rolled loosely to fill the whole bore of the tube. The space within the tube above the coil was filled with fibrous asbestos, as a precaution against possible explosions, though none ever occurred.

The aspirated air, after being first dried by sulphuric acid, was passed rapidly through the liquid with whose vapours it was to be charged. The liquid was placed in a round-bottomed flask supported at such a height that a water-bath might be brought under it to raise the temperature, if desired. An exit-tube passing through the stopper of this flask conveyed the mixture of air and vapour into the combustion tube. The latter was drawn out and bent at its lower end so as to just dip beneath the surface of 50 c.c. of distilled water in the first of a series of four condensing bottles, each of which also contained water through which the gaseous combustion products were made to pass. Whenever a new vapour was to be burned, some preliminary experimenting was required to find the best temperature at which to maintain the evaporating liquid, and the proper rate at which to draw air through it. After the best conditions had been once ascertained, however, the combustion usually proceeded smoothly and with very little separation of carbon, the copper roll often maintaining its dull red glow for several hours without requiring any special attention from the experimenter. A few moments' application of a Bunsen burner flame was frequently quite sufficient to start the reaction, though there were cases in which the heating had to be continued for more than fifteen minutes. The ratio between air and vapour in the different experiments could not readily be kept constant, and bore no known relation to the theoretical quantities corresponding to any particular chemical equations. The composition of the mixtures and the rate of aspiration were simply such as experience showed were favourable to uninterrupted combustion. In experiments with the same substance the largest yields of aldehyde were often obtained when only half the roll was glowing.

Considerable time was spent in the search for a reliable analytical method for the determination of small quantities of formic aldehyde in presence of much acetic aldehyde. In the course of this search Mr. Brown studied nearly all the methods that have been proposed for the analysis of formic aldehyde solutions, and came to the conclusion that acetic aldehyde must always first be removed. The method of separation which was adopted was based on the fact, referred to in the article by Mulliken and Scudder, that acetic aldehyde may be completely boiled out from dilute aqueous solu-

* Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology. From the *American Chemical Journal*, xxv., No. 2.

† Volume xxiv., p. 446. Attention is here called to two slight corrections that should be made in the text of the article quoted. On page 451, line 21, insert the words, "containing strong sulphuric acid," between "second tube" and "held"; and on p. 452, line 18, read "tertiary," between "secondary" and "and butyl."

tions in such a way that practically all of the formic aldehyde will be held back by the water. To accomplish this result in the present instance, the liquid contents of all the condenser bottles were united, diluted to 500 c.c. with water, and placed in a round-bottomed litre flask connected with a long upright return-flow condenser. The upper end of the condenser was joined, by means of a descending glass tube, with a glass worm packed in ice and salt. The worm delivered into a flask surrounded by a freezing-mixture. The dilute aldehyde solution was gently boiled for two hours to drive over the acetic aldehyde. During the boiling, warm water at 45° to 50° was kept circulating through the condenser, the temperature being carefully controlled with the aid of a thermometer hung within the glass condenser jacket. It was found, by direct experiments, that the quantity of formic aldehyde vapour which passed over and was absorbed by water placed in the cooled receiver upon boiling a 1 per cent aqueous solution for two hours, as above described, was too small to be accurately determined, though its presence in the receiver could be shown qualitatively by the delicate gallic acid test. The removal of acetic aldehyde by the process was so complete that in the experiment on the oxidation of ethyl alcohol, in which 43 grms. of acetic aldehyde were produced, no trace of acetic aldehyde could be detected in the flask at the close of the two hours' boiling. A strong, unmistakable formalin odour was, however, noticeable in each of the warm boiled solutions in which formic aldehyde was determined. These solutions also all gave very pronounced qualitative reactions for formic aldehyde, by the gallic acid, resorcin, and hexamethylenetetramine tetra-bromide tests.

The determinations of formic aldehyde which follow were made by the colorimetric method of Trillat in essentially the form described by Wolff (*Ztschr. d. Nahr. u. Genuss.*, 1890, 89), though with certain added precautions.

The determinations of acetic aldehyde were obtained by the colorimetric method of Thresh (*Pharm. Journ.* [3], ix., 408), which was so far modified and improved as to give results which are trustworthy to within 2 per cent of their total value. Acetic aldehyde was tested for in all oxidation-products by adding solid sodic hydrate to a few centimetres of the mixed and diluted aqueous solutions until the liquid became almost syrupy, and then boiling for a minute or two. The least trace of acetic aldehyde then gave the characteristic aldehyde resin odour, and a deep yellow solution.

The compounds chosen for oxidation were Kahlbaum's best preparations, and were carefully rectified before use by distillation through a tall Le Bel-Henninger tower. Only the middle portion of a large fraction of correct and constant boiling point was used, unless it is otherwise stated in the record of the experiment. In the following brief statement of results the compounds studied follow one another in an order which corresponds to the quantity of formic aldehyde produced by their respective oxidations, the substance giving the largest yield closing the list. The experiments on acetone and ethyl alcohol were made by Mr. Brown, the remainder by Mr. French.

Summary of Experimental Results.

Acetone.—(Prepared from the pure bisulphide compound). 271 grms. gave 0.6055 gm. formic aldehyde, but no acetic aldehyde. Duration of oxidation, two and a half hours. Temperature of bath, 25° to 30°.—*Yield of formic aldehyde, 0.22 per cent.*

Ethyl Alcohol.—(Prepared from the purest absolute alcohol).—187 grms. gave 0.832 gm. formic aldehyde and 42.9 grms. acetic aldehyde. Duration of oxidation, three hours. Temperature of bath, 35° to 40°.—*Yield of formic aldehyde, 0.44 per cent.*

Pentane.—(Boiling point 35° to 37°). 119 grms. gave 1.05 grms. formic aldehyde, but no acetic aldehyde. No bath was employed.—*Yield of formic aldehyde, 0.88 per cent.*

Acetic Acid.—("99 to 100 per cent 'Kahlbaum's acid' free from homologues"). 232 grms. with the bath at 60° to 65° gave 1.95 grms. formic aldehyde, but no acetic aldehyde. The oxidation was very easily controlled and the copper roll no more disintegrated than in other experiments. Most of the unoxidised acid in the distillate was neutralised with calcium carbonate before determining the aldehyde.—*Yield of formic aldehyde, 0.84 per cent.*

Ethyl Oxide.—(Absolute ether distilled from sodium, boiling between 35° and 36°). 258 grms. gave 4.78 grms. formic aldehyde and 12.24 grms. acetaldehyde.—*Yield of formic aldehyde, 1.86 per cent.*

Amylene.—(Mainly trimethylethylene. Boiling point 37° to 40°). 100 grms. gave 2.01 grms. formic aldehyde, but no acetic aldehyde. No bath was used.—*Yield of formic aldehyde, 2.01 per cent.*

Normal Propyl Alcohol.—Boiling point 96° to 99°. 56 grms. with the bath at 45° to 50° gave 1.53 grms. formic aldehyde, but no acetaldehyde.—*Yield of formic aldehyde, 2.72 per cent.*

Trimethylcarbinol.—(Boiling-point 82° to 85°). 39 grms. gave 2.01 grms. formic aldehyde, but no acetaldehyde. Temperature of bath, 35° to 40°. The quantity of carbon dioxide formed in the experiment was unusually large.—*Yield of formic aldehyde, 5.17 per cent.*

An oxidation of 150 grms. of benzene, free from thiophene, with the bath at 45° to 50°, did not give formic aldehyde in determinable quantity. The oxidation of an equal weight of toluene gave very appreciable quantities of formic aldehyde, but quantitative determinations were not attempted, as it was found that benzoic aldehyde, which was also present, would prevent the successful employment of the Trillat method.

In comparing the yields of formic aldehyde obtained in these experiments, it must be remembered that the values recorded hold true for a single set of conditions only, and that these cannot always have been the most favourable ones possible. The important fact demonstrated is the marked tendency to the production of measurable quantities of formic aldehyde in the partial combustion of numerous carbon compounds belonging to very dissimilar types. So far as yet appears, this reaction is even of more frequent occurrence in such oxidations by air and copper oxide as have been described, than is the more familiar formation of oxalic acid in oxidations by nitric acid. Whether formic aldehyde, in small quantities, is also a frequent product of oxidations in the wet way, we have not attempted to determine. That it may be formed in many reactions of this class is, however, not in the least improbable.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 6).

PART II.—THE CHARACTERS OF THE STONES.

The Crust.

The crust is brownish-black to black in colour; it is mostly smooth, but in parts is scoriaceous or wrinkled; it shows occasional protuberances. The crust is dull, but a spot, 7 m.m. in diameter, on Stone No. 7 is lustrous; in the case of Stone No. 3 a patch of crust, 3 m.m. by 4 m.m. is transparent, and of a light green colour. On Stone No. 7 there is a linear ridge which can be traced

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

round one of the edges of the stone for a distance of 70 m.m.; a fracture of the crust shows that the ridge is the prolongation of a black vein in the stone. The thickness of the crust averages 0.5 m.m., and reaches a maximum of 1 m.m.

Each of the stones Nos. 9 and 10 has one side different in aspect from the others; instead of being comparatively uniform in curvature, this side is covered with pit-like depressions.

The Fractured Surfaces.

The fractured surface of Stone No. 7 shows part of a broken troilite-nodule, 5 m.m. wide, of irregular form; an unbroken chondrule, 2 m.m. in diameter, projects above the general surface; in one part is a material of vitreous lustre, curved, nearly linear, and 2 m.m. long.

A freshly made fracture of Stone No. 3 varies in parts from white to whitish-grey in colour; one portion shows a dark grey oval patch, 12 m.m. by 7 m.m.; another was found to break through a beautifully regular bluish or bluish-grey chondrule, 2½ m.m. in diameter.

Specific Gravity.

The specific gravity was determined for a fragment, weighing 13.8522 grms., of Stone No. 3; the fragment was free from crust, and exactly similar in aspect to a fragment of the same stone used for chemical analysis. The loss of weight in distilled water at 20.2° C. was 3.8973; the air was extracted from the pores by the air-pump. Duly corrected, the weight of 1 c.c. at 20.2° C. is 3.545 grms.

Microscopic Examination.

Thin sections prepared for the microscope, when examined with the unassisted eye, by reflected light, show small, very irregularly shaped, lustrous, metallic constituents (nickel-iron), and also still smaller dull opaque black particles (completely enclosed nickel-iron, troilite, or chromite), dispersed through a greyish-white stony material; one of the five sections shows part of a black vein. By ordinary transmitted light the stony material is seen with the aid of the microscope, to consist almost wholly of a nearly colourless crystalline groundmass, constituted of crystals which are chiefly small and rarely show any boundary due to the section of a natural face. Between crossed Nicols the groundmass (olivine, enstatite, and plagioclasic feldspar), is seen as a bright small-grained mosaic (grey, yellow, red, blue, and green), interspersed with small and large crystals (the latter chiefly olivine); here and there, small quantities of a mineral nearly or quite free from cracks, and polarising in grey tints (probably plagioclasic feldspar) fill up intervening irregular spaces, and mould the other crystallised material; the general aspect being very like that of sections of the meteorites of Lind County, Grossliebenthal, Girgenti, and Alfianello. Enclosed in the groundmass, and intimately connected therewith, are some chondrules, few in number, and almost all of them white. One of them is perfectly round, and has a well marked shell, the whole of the kernel and the shell extinguishing the light simultaneously (monosomatically), and being constituted apparently of short blocks, characters which are very common in olivine-chondrules: further, as is not unusual, particles of nickel-iron are closely grouped round the greater part of the outer boundary of the shell. A second chondrule is very similar, but no shell is evident, and the block-structure is less marked. A third chondrule, almost monosomatic, shows a triple shell. Other chondrules are polysomatic, being composed of several crystals having different optic orientations. In each of two slides is a section of a chondrule, which, looked at with the unassisted eye, is black by reflected light; with the microscope and crossed Nicols, it is seen to consist of a transparent substance polarising in grey tints (probably plagioclasic feldspar) and enclosing opaque particles which are densely packed in the centre, and are almost absent near the circumference of the chondrule; a similar black chondrule is

shown by a section of the Grossliebenthal meteorite. Some patches of material seen in the sections are micro-crystalline aggregates, and are possibly enstatite.

CHEMICAL EXAMINATION.

As there is necessarily more or less speculation in the interpretation of the results observed during the chemical examination of a mechanical mixture of compounds having one or more chemical elements in common, the observations and calculations are conveniently kept quite distinct from each other, and recorded in separate sections. Both are given in detail, so that future investigators of meteoric stones may know the kind of difficulty which presents itself in such an inquiry, and may form an estimate of the weight to be assigned to the numerical results arrived at.

SECTION I.—OBSERVATIONS.

Weights obtained in the Course of the Chemical Analysis.

Magnetic Separation.

1. A freshly broken, easily frangible, crustless fragment of Stone No. 3, weighing 14.6 grms., was crushed in a steel mortar, and afterwards pulverised, in small portions at a time, in an agate mortar; it was impossible, owing to the presence of malleable grains of nickel-iron alloy, to reduce the material in this way to a fine powder of uniform composition. The alloy was next magnetically extracted by means of a seven-toothed iron comb, such as is used by grainers, but which had been magnetised; the powder being worked through in small quantities at a time. The residual powder was again pulverised in the agate mortar and the magnetic separation repeated. At the end of a series of operations the material had been divided into two parts; the one, attracted, weighing 2.0144 grms.; the other, unattracted, weighing 12.4208 grms.; the total quantity of material available for analysis being thus 14.4352 grms. The attracted material consisted of particles of different sizes; some of them were about a millimetre in diameter; much of the remainder consisted of smaller but still coarse grains, and another portion consisted of particles which were extremely minute, and thus readily oxidisable on exposure to air or moisture; the unattracted material was an impalpable powder of a bluish-grey colour and apparently quite free from iron-rust.

Attracted Material: Total Weight, 2.0144 Grms.

Treatment with Solution of Mercuric Ammonium Chloride.

2. 0.7421 grm. of the attracted material was transferred to a small flask, and treated with cold mercuric solution in an atmosphere of hydrogen as described in a previous paper (*Mineralogical Magazine*, 1894, vol. x., p. 293), the flask and contents being frequently shaken during the day-time; after the action had proceeded for some time, the liquid was quickly filtered, and the insoluble matter was washed with cold water which contained a little mercuric solution, and had been boiled to expel dissolved air. For each of the first two extractions 200 c.c. of the mercuric solution were used; for each of the next five, 100 c.c.; the first extraction was allowed to proceed for three hours; each of the next four, for twenty-four hours; the sixth, for ninety-six hours; and the seventh, for twenty-four hours.

Each of the extracts was acidified, heated to boiling, and precipitated by sulphuretted hydrogen, and the several filtrates were evaporated to dryness. The residue from the third extract showed by its colour that an appreciable amount of alloy had been extracted by the mercuric solution, and there was still an evident tinge of colour even in the residue from the seventh extract; the colouration was much smaller in the case of the fourth and fifth extracts than in that of the third, while those of the sixth and seventh, though evident, were only just appreciable; the last two were of about equal intensity, although the sixth extraction had occupied four days, and the seventh only one. There was by this time much admixed mercury and mercurous chloride, protecting the material to some extent from the action of the solvent; possibly, also, some of the

particles of the alloy were so large as to require a very prolonged action to produce solution; possibly some had been superficially oxidised, and were partially sheltered by the oxide from contact with the liquid; undissolved particles of alloy are very liable to be superficially oxidised when exposed to the air during the filtration. The extraction, although incomplete, was accordingly not further proceeded with at this stage.

The various precipitates produced by the sulphuretted hydrogen were ignited, and the mercury driven off; there remained a small brownish residue, which was soluble in warm hydrochloric acid, and gave a rich yellow solution; it was again precipitated by sulphuretted hydrogen, and the filtrate, which may contain a little iron carried down by the mercuric sulphide, was added to the main extracts. The brown precipitate weighed after ignition 0.0001 grm., and was found to be due to the presence of copper. The extracts having been collected together, the iron was oxidised, and at the same time the ammonium chloride decomposed, by evaporation with strong nitric acid; the residue was then treated with strong hydrochloric acid, and again evaporated to dryness. From the dilute solution the iron was separated from the nickel by a fourfold precipitation with sodium acetate; probably two precipitations would have sufficed, for it was afterwards found that the nickel separated by the third and fourth precipitations were scarcely large enough to be appreciable. After a final precipitation with ammonia and ignition, the precipitate weighed 0.4933 grm. Of this 0.4054 grm. was ignited in a current of hydrogen, and treated with hydrochloric acid; the insoluble SiO_2 weighed 0.0028, and was probably due to the action of the voluminous boiling liquid on the glass during the four precipitations of the iron. The dissolved iron was precipitated by ammonium sulphide, and the filtrate, which showed no trace of nickel (thus indicating the completeness of the separation from that metal), was evaporated to dryness; the ammoniacal salt was expelled by gentle ignition; from the residue then obtained, a small quantity of phosphorus (presumably due to oxidation of schreibersite, phosphide of iron, and nickel) was eventually separated by molybdic solution, and afterwards by magnesia mixture; the $\text{Mg}_2\text{P}_2\text{O}_7$ weighed only 0.0005.

The nickel and cobalt were twice precipitated by caustic potash and bromine water; as oxides they weighed 0.0606, as metal 0.0487. The cobalt was separated from the nickel by the nitrite method, and converted into potassium cobalt sulphate ($3\text{K}_2\text{SO}_4 \cdot 2\text{CoSO}_4$); this weighed 0.0166.

3. The residue from the action of the mercuric solution was in two parts; one part, still adherent to the filter, weighed after ignition (and therefore partial oxidation), 0.0019 grm.; the other part, which had been washed from the filter, contained some bright metallic spangles (probably schreibersite, phosphide of iron, and nickel), mingled with much mercurous chloride, mercury, and coarse grains of silicate; further, much of the material was found to be still magnetic; after being heated in a current of hydrogen to a temperature just below visible red heat until no further volatilisation took place, it weighed 0.3366 grm. The residual powder, instead of consisting of light coloured silicates, as had been expected, was almost wholly of a dull black colour, but further contained the lustrous metallic spangles already referred to; and the whole was attracted by the compass-needle, showing that the coarse grains of silicate, obviously present, themselves contained magnetic matter. It was inferred that the powder consisted largely of magnetic oxide of iron; the residue was therefore heated to low redness in a current of hydrogen, again submitted to the action of the mercuric solution, transferred back to the boat, and again heated in hydrogen; as the residue was not much diminished and was still of a dull black colour, the operations were repeated, the temperature being raised to full red heat, but with a similar result. After a further extraction with mercuric solution, the residue was again heated in hydrogen to a full red heat, and weighed (0.2759 grm.)

The part adherent to the filter weighed, after ignition, 0.0091 grm. The combined extracts yielded, after a double precipitation with sodium acetate, Fe_2O_3 0.0439, and $\text{Ni}(\text{Co})$ 0.0135.

4. As the total residue had only been reduced by the last operations from 0.3366 grm. to 0.2850 grm., and was not appreciably changed in aspect, it was decided to treat the residue with hydrochloric acid, and to analyse it in the same way as the unattracted material.

0.2757 grm. was treated on the water-bath with dilute HCl (s.g. 1.06); there was immediate effervescence, which lasted for ten minutes. From this it is inferred that particles of alloy had been protected from the mercuric solution by a coating of oxide or by enclosure in grains of olivine silicate, probably in both ways. The silica set free by the acid was separated by means of sodic solution, and weighed (0.0447 grm.). The residue washed from the filter weighed 0.1230, and was white; the part adherent to the filter weighed, after ignition, 0.0129 grm.

From the acid solution the following weights were obtained:—

$\text{Fe}_2\text{O}_3, \text{SiO}_2$ 0.0450 (yielding SiO_2 0.0013, presumably due to the action on the vessels).

$\text{Ni}(\text{Co})\text{O}$ 0.0088; yielding $\text{Ni}(\text{CO})$ 0.0072.

CaO 0.0036, probably almost entirely due to the action on the glass and porcelain during the precipitation of the iron and the separation of the nickel.

$\text{Mg}_2\text{P}_2\text{O}_7$ 0.1137.

Unattracted Material: Total Weight 12.4208 Grms.

Extractions with Water, Alcohol, and Ether.

5. 1.0017 grms. of the unattracted material was transferred to a platinum dish, and covered with 100 c.c. of distilled water; after being boiled the solution was allowed to cool, and then filtered without prolonged standing; the filtrate was opalescent. It was evaporated to dryness, 100 c.c. of water was again added, and the liquid was boiled. It was afterwards filtered, the filter being on this occasion being unwashed; the filtrate was now limpid, and yet contained all the soluble matter; the powder adherent to the dish and filter was doubtless finely divided silicate which had been in a state of suspension, and had caused the opalescence. The soluble residue yielded by the evaporation of the filtrate weighed 0.0026 grm., or 0.26 per cent.

Its solution was inactive to litmus and turmeric, and gave a rich yellow colour to the Bunsen flame. On spontaneous evaporation it began to deposit a precipitate as soon as it became concentrated, the liquid becoming quite milky in appearance when its volume had decreased to a cubic centimetre; after the evaporation was complete, the residue, examined with the microscope, was seen to consist mostly of small crystals optically isotropic, but of no distinct form; there were a few isolated groups of radiating birefringent plates, and also some isolated acicular crystals having straight extinction. The solution gave no precipitate with ammonia and ammonium chloride, even on boiling, but was found to contain calcium and a minute amount of magnesium. It contained sulphate in considerable quantity, but only an extremely minute trace of chloride; no phosphate could be detected. This is virtually the same result as was obtained in the examination of the Makariwa stone (*Mineralogical Magazine*, 1894, vol. x., p. 297); in that case it was inferred that the salts found in the extracting water were due to a partial oxidation of the protosulphide of iron (troilite) to sulphate, and to the subsequent action of the dissolved sulphate on the silicates, but it was uncertain whether the oxidation had taken place during the aqueous extraction itself or while the stone was lying buried in the ground. As the Zomba stone was quite fresh, it may be concluded that the oxidation of the troilite takes place during the boiling, and that the soluble salts may be accounted for without being regarded as original constituents of the meteoric stone.

The residue left after treatment with the distilled water

(To be continued).

Ordinary Meeting, June 20th, 1901.

(Concluded from p. 10).

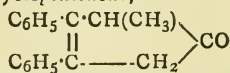
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} \rangle \text{CH}_2 \cdot$$
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \overset{\alpha}{\text{CH}} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \underset{\beta}{\text{CH}_2} \end{array} \rangle \text{CO.}$$
$$\begin{array}{l} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} \rangle \text{CO}$$
$$\begin{array}{l} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ | \qquad \qquad \qquad \diagup \text{CO} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array}$$
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$$

The authors show that the sparingly soluble monalkyl homologues of anhydracetonebenzil prepared by Japp and

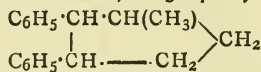
Burton by heating a mixture of benzil and homologues of acetone with aqueous potassium hydroxide, belong to the β -series, and that readily soluble α -isomerides, overlooked by these authors, are formed in small quantity at the same time. By using cold alcoholic potassium hydroxide as a condensing agent, the α -compounds may be obtained in larger quantity. All the α -compounds are distinguished by forming benzylidene derivatives when treated with benzaldehyde and alcoholic potassium hydroxide.

With benzil and alcoholic potassium hydroxide, α -methylanthracetonebenzil yields α -methylanthracetonebenzil, $C_{32}H_{26}O_4$ (dimorphous; silky needles, m. p. 185° ; and warty crystals, m. p. 194°), which is obtained in the form of a complex potassium salt, $C_{32}H_{25}O_4K, C_{32}H_{26}O_4, 4C_2H_5OH$. The sodium salt may be obtained directly from benzil and methyl ethyl ketone by condensation with alcoholic sodium ethoxide. α -Methylanthracetonebenzil is ethylated by boiling it with alcohol and sulphuric acid, yielding the compound $C_{32}H_{25}(OC_2H_5)_3$ (short needles, melting at 250°).

Both α - and β -methylanthracetonebenzil are transformed, by brief boiling with hydriodic acid, into the same methylphenylcyclopentenone,—



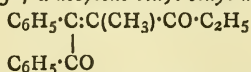
(faint yellow, oblique, flat prisms or plates, m. p. $77-78^\circ$), which yields a phenylhydrazine, $C_{24}H_{22}N_2$, melting at $145-152^\circ$. By boiling α -methylanthracetonebenzil for five hours with hydriodic acid and red phosphorus, the methylphenylcyclopentenone, which is first formed, is in its turn reduced to 1-methyl-2:3-diphenylcyclopentane,—



(m. p. $62-63^\circ$), already obtained by Japp and Murray (*Trans.*, 1897, lxxi., 153), by the reduction of α -anhydrobenzillævulic acid, the carboxyl group being eliminated in the latter case.

By boiling with slightly diluted sulphuric acid, or with glacial acetic acid, α -methylanthracetonebenzil yields a dehydration product, $C_{26}H_{28}O_2$ (m. p. 230° , with evolution of gas. β -Methylanthracetonebenzil, when heated with formic acid, gives the same product.

In addition to the foregoing, the following compounds have been prepared:—Benzylidene- α -methylanthracetonebenzil, m. p. 225° ; α -desylene-ethyl ethyl ketone,—



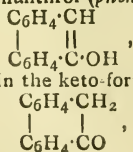
m. p. 128° , converted, on heating, into $\alpha\beta$ -dimethylanthracetonebenzil, m. p. 150° ; $\beta\beta$ -dimethylanthracetonebenzil, m. p. 181° ; α -ethylanthracetonebenzil, m. p. 114° , and its benzylidene derivative, m. p. 178° ; $\alpha\beta\beta$ -trimethylanthracetonebenzil, m. p. 131° ; α -propylanthracetonebenzil, m. p. 89° ; and its benzylidene derivative, m. p. 166° ; β -propylanthracetonebenzil, m. p. 152° ; $\alpha\beta$ -diethylanthracetonebenzil, m. p. $113-114^\circ$; α -amylanthracetonebenzil, m. p. 57° ; and its benzylidene derivative, m. p. 156° .

All β -monalkylanthracetonebenzils corresponding with these α -compounds, but not included in the foregoing list, have been already described by Japp and Burton (*loc. cit.*).

The oxidation products of the various methylanthracetonebenzils are at present under investigation.

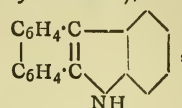
120. "Formation of Carbazoles." (A Preliminary Note). By F. R. JAPP, F.R.S., and W. MAITLAND, B.Sc.

The fact that β -phenanthrol (phenanthrene),—

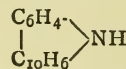


interacts, apparently in the keto-form,—

with phenylhydrazine, eliminating simultaneously water and ammonia, and yielding 2':3'-diphenyleneindole (phenyl β -phenanthrylcarbazole),—



as in E. Fischer's synthesis of indoles (compare Japp and Findlay, *Trans.*, 1897, lxxi., 1117), led the authors to try whether β -naphthol, which β -phenanthrol in many respects resembles, would behave in an analogous manner. On heating β -naphthol with excess of phenylhydrazine there was no reaction, but on adding to the mixture some phenylhydrazine hydrochloride and continuing the heating, water, and ammonia were evolved, and a fair yield of a phenyl- β -naphthylcarbazole,—

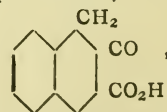


(needles melting at $134-135^\circ$), was obtained. The reaction does not take place when β -naphthol is heated with phenylhydrazine hydrochloride alone.

The following derivatives of this carbazole were prepared and analysed:—Nitroso-derivative, yellow flat needles, m. p. $144-145^\circ$ (with decomposition); acetyl derivative, small pearly laminae, m. p. 149° ; benzoyl derivative, slender needles, m. p. 189.5° .

Two phenyl- β -naphthylcarbazoles—the number predicted by theory—are already known; one melting at 330° , isolated by Graebe and Knecht from coal-tar, and afterwards synthesised by them by passing the vapour of phenyl- β -naphthylamine through a red-hot tube (*Annalen*, 1880, ccii., 1); and a second obtained by Schöpf (*Ber.*, 1896, xxix., 269), by elimination of carbon dioxide from phenyl- β -naphthylcarbazolecarboxylic acid, and asserted by him to melt at 120° . The melting-points of the derivatives are given by Schöpf as follows:—Nitroso derivative, 132° ; acetyl derivative, 142° ; benzoyl derivative, 170° . With the exception, however, of these very considerable differences in the melting-points, the descriptions given by Schöpf of his compounds would apply to those prepared by the authors; moreover, various colour reactions which he mentions are the same in both cases. The authors, therefore, prepared Schöpf's phenyl- β -naphthylcarbazole by his method, and found that it melted at $134-135^\circ$ (instead of at 120° , as stated by him), and was absolutely indistinguishable from their compound. As the yield by Schöpf's method is very poor, they did not trouble to prepare the derivatives over again from substances obtained in this way; but they have no doubt that similar errors in the determination of the melting-points have been committed by the German investigator in the case of these also.

Schöpf obtained his phenyl- β -naphthylcarbazole carboxylic acid by heating 3-hydroxy- β -naphthoic acid (m. p. 216°) with phenylhydrazine, a reaction which would correspond with that described by the authors, except that this so-called hydroxynaphthoic acid is the keto-form dihydro-2-keto-3-naphthoic acid,



and that the addition of phenylhydrazine hydrochloride is unnecessary.

α -Naphthol, when heated with the mixture of phenylhydrazine and its hydrochloride, yielded phenyl- α -naphthylcarbazole (m. p. 225.5°), already obtained by Kym (*Ber.*, 1890, xliii., 2465), by desulphurising thiophenyl- α -naphthylamine with finely divided copper. The present reaction does not take place so readily as with β -naphthol, and the yield is small.

The authors are engaged in extending this reaction to other phenols, and to other arylhydrazines in presence of their hydrochlorides.

121. "*Metal-ammonia Compounds in Aqueous Solution.* Part III. *Solutions of Salts of the Alkaline Earth Metals.*" By H. M. DAWSON and J. MCCRAE.

The distinction of ammonia between solutions of salts of the alkaline earth metals and chloroform has been determined at 20°, and the results obtained indicate that the calcium ions form complex ammonia ions to a slight extent in solution, whilst the strontium ion possesses the power of fixing ammonia in a less degree, and the barium ion has the lowest power.

122. "*Metal-ammonia Compounds in Aqueous Solution.* Part IV. *The Influence of Temperature on the Dissociation of Cupri-ammonia Sulphate.*" By H. M. DAWSON and J. MCCRAE.

The distribution of ammonia between water and chloroform, and between aqueous copper sulphate and chloroform has been determined at 10° and 30°. The results indicate that the copper sulphate fixes more ammonia at the lower than at the higher temperature; but no exact quantitative statement can be made as to the influence of temperature on the dissociation of the compound $\text{Cu}_4\text{NH}_3\text{SO}_4$, since within the limits of temperature at which the experiments were made this influence is very small.

The same relationship between ammonia concentration and distribution coefficient has been found at 10° and 30° as that previously observed at 20° (*Trans.*, 1901, lxxix., 496).

123. "*On the Combined Action of Diastase and Yeast on Starch-granules.*" By G. H. MORRIS, Ph.D.

When yeast is allowed to act on a solution of starch-conversion products in the presence of active diastase, the quantity of matter fermented is greatly in excess of that which can be fermented by the yeast alone; and when active diastase and yeast are allowed to act conjointly on the so-called stable-dextrin, which under ordinary conditions is neither degradable by diastase nor fermentable by yeast, it is entirely fermented.

It is now shown that a similar action takes place when certain ungelatinised starch-granules are submitted to the joint action of malt extract and yeast, the quantity of starch decomposed by the joint action being about three times that dissolved by malt-extract alone. The increased action in the presence of yeast is not due to the removal of the soluble product, maltose, from the field of action, and the consequent greater activity of the diastase. No increased diastatic action takes place in the presence of yeast if the fermentative power of the latter is checked by chloroform, neither does any increase of action take place when the malt-extract is submitted to fermentation, and the yeast-cells removed, before the addition of the starch-granules.

Precipitated diastase behaves in the same way as cold water malt-extract, but to a lesser extent.

The combined action of diastase and yeast only occurs with those starches which are attacked in the ungelatinised form by diastase, such as barley or malt starch. The granules of potato starch are not acted on by diastase even in the presence of yeast.

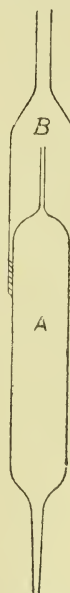
124. "*A Calibrating Mercury Pipette.*" By C. A. BELL, M.B.

The little device figured in the diagram will be found very useful in calibrations of all kinds. It is easily constructed on any scale; the volume of mercury delivered by it is for all practical purposes constant, and the time saved by its use is considerable.

The mercury reservoir, A, is made from a piece of soft German or soft Jena tubing, of moderate wall thickness, and free from internal flaws. At the lower end it is drawn out to a narrow tube terminating in an orifice about 0.4 m.m. in diameter. The edge of this orifice may be slightly fused, but not so as to invert it. At its upper end, A is drawn

out to a very fine capillary tube, which should be of such diameter at its narrowest section that a pressure of at least 15 c.m. of mercury is required to drive the metal through it. A short tube of such narrow bore is not easily prepared in an ordinary blowpipe or Bunsen flame; the final drawing may, however, be easily effected in the outer mantle of a candle-flame, as in preparing a Lippmann's capillary electrometer. The little tube so formed should be cut at such a point that the diameter of the portion left on A (from 1 to 1.5 c.m. in length), diminishes continuously from A to the end. A constantly increasing pressure is then required to drive mercury nearer and nearer to the orifice.

The reservoir A thus prepared is cemented, as shown, air-tight into a somewhat wider tube, B, which is drawn out at its upper end so that an india-rubber tube may be attached to it. The cement used may be sealing-wax, but if B is just wide enough to receive A, a much neater joint may be made with fused silver chloride. A little of the chloride is melted in a porcelain crucible, and the well heated end of B dipped into it repeatedly until a sufficient quantity of the chloride has been collected. That which adheres to the inner surface of B is removed with a penknife; the previously warmed end of A is then passed into B, and the two tubes heated together high above a Bunsen flame, to avoid reduction of the silver, until the chloride melts. When prepared in this way, the pipette may be heated and dried by a current of air, if necessary, without disconnecting A and B.



To use the pipette, an india-rubber tube of some length is slipped over the narrow end of B, and secured air-tight by a few turns of soft copper wire, the ends of the wire being left loose. The point of the pipette is then plunged well below the surface of mercury contained in a bottle or basin, and suction applied until the metal rises to within a couple of millimetres of the capillary orifice. If the capillary tube has been properly formed, it can, without the slightest difficulty, be brought to any desired level which may be marked on the outside of B; but generally it is sufficient to bring it within a short distance of the orifice. A rather coarse capillary measured by a microscope micrometer was found to have, at the orifice, a diameter of 0.008 c.m. The capacity of a tube of this diameter is only 0.00005 c.c. per centimetre of length, so that a variation in the level of a millimetre either way is of small importance.

The filling having been accomplished, the rubber tube

is pinched; the pipette may then be lifted and carried about without the loss of a particle of mercury, so long as it is held in a nearly vertical position. Inclining it, however, by increasing the effective pressure on the capillary, may cause mercury to pass from A to B. This is much less likely to happen when in the process of filling the mercury has not been drawn right up to the orifice; the pressure may then increase or diminish considerably without causing the escape of mercury from either end of A.

In discharging the pipette, the pressure of the fingers on the rubber tube having been released, the mercury is allowed to trickle gently down the side of the tube or vessel to be calibrated. Usually a short thread of metal remains in the lower prolongation of A; this is best removed by pinching the rubber tube near its open end with the fingers of the hand holding the pipette, and compressing it about its centre with the other hand. It is not advisable to blow into B, as in the course of a calibration moisture from the breath may find its way into A, causing the formation of air bubbles within it.

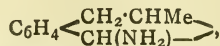
As air bubbles never form in A when the mercury entering it is dry and free from surface impurities, any sensible variation in the volume delivered at constant temperature can be due only to variations in the point at which disruption occurs in the mercury when the pipette is raised. These, however, are exceedingly small. In a series of tests with a pipette holding about 17 grms. of mercury, and having an outflow orifice of 0.05 c.m. in diameter, the weight of mercury delivered was constant within 0.0005 grm., or in volume 0.00004 c.c. By making the outflow orifice very small, still greater constancy can be secured; but the time occupied in charging and emptying is then greatly increased. In conducting a test of this kind, of course the temperature of the mercury must be carefully observed. Mercury contained in a bottle or jar can never be assumed to be at room temperature, and when poured into a basin its temperature may alter rapidly from a variety of causes.

Sometimes a small globule of metal sticks very persistently in the lower constricted part of A. Such a globule can usually be rinsed out by sucking back a little of the metal already delivered, especially if the part of the tube containing it has been previously warmed.

The advantages of this pipette over Bunsen's well-known calibrating device are obvious. The quantity of mercury required for any calibration is a minimum; the metal need never be touched by the fingers; and as surface impurities are excluded by the pipette, which acts as a filter, the mercury delivered by it is always bright and clean, and lies in perfect contact with the wall of the receiving vessel.

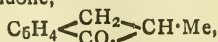
125, "*α*-Amido-*β*-methylhydrindene." By F. S. KIPPING and G. CLARKE.

The authors have prepared *α*-amido-*β*-methylhydrindene,—



in order to study the salts obtained by combining it with various optically active acids, and thus perhaps to elucidate the curious behaviour of its lower homologue hydrindamine (Kipping, *Trans.*, 1900, lxxvii, 861; and Kipping and Hall, *Trans.*, 1901, lxxix, 442).

β-Methylhydrindone,—



is easily obtained by the action of aluminium chloride on *α*-methylhydrocinnamic chloride, ring formation taking place with the elimination of hydrogen chloride (compare Kipping, *Trans.*, 1894, lxxv, 680; Kipping and Hill, *Trans.*, 1899, lxxv, 144; and Kipping and Hunter, *Trans.*, 1901, lxxix, 604).

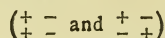
This method gives much better results than the treatment of the acid with concentrated sulphuric acid (von Miller and Rhode, *Ber.*, 1890, xxiii, 1888), the yield being from 70 to 80 per cent of the theoretical.

β-Methyl-*α*-hydrindoxime crystallises in well-defined octahedra, melting at about 103°. The base, of which the formula is given above, is obtained by reducing the oxime with sodium amalgam in dilute acetic acid solution. It resembles hydrindamine in general properties.

Since *α*-amido-*β*-methylhydrindene contains two asymmetric carbon groups, it should consist of four optically different forms, and when combined with optically inactive acids it might be expected to give rise to two series of salts.

As a matter of fact, on fractionally crystallising the hydrochloride of the original base from water, it is resolved into a sparingly soluble salt, which forms long, silky needles, decomposing at about 252°, and a readily soluble salt which is obtained in small, ill-defined nodular masses decomposing at about 225°.

The two hydrochlorides are probably the salts of the two externally compensated



bases, but the more readily soluble one may not be quite free from its isomeride. The sparingly soluble salt gives a *platnichloride*, $(\text{C}_{10}\text{H}_{13}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$, which crystallises from water in lustrous, yellow plates, decomposing at about 192°, whilst the readily soluble isomeride gives a *platnichloride*, $(\text{C}_{10}\text{H}_{13}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, which is anhydrous, and decomposes at about 202°.

The *benzoyl* derivative prepared from the sparingly soluble hydrochloride crystallises in silky needles, melting at 169°, whereas the corresponding compound, obtained from the readily soluble hydrochloride, melts at about 138°.

The *sulphate* of the original base crystallises in large transparent prisms, and does not seem to be resolved into different products when fractionally crystallised from water.

The investigation of these bases is being continued.

126, "*Stereoisomeric α- and α'-Sulphonic Derivatives of Camphor.*" By H. E. ARMSTRONG and T. M. LOWRY.

The authors have further examined Reychler's camphor-sulphonic acid, prepared by sulphonating camphor by means of a mixture of sulphuric acid and acetic anhydride; they have also prepared corresponding acids from chloro- and bromo-camphor, which are reducible to Reychler's acid. They confirm Reychler's observation that two camphorsulphonamides are formed by the action of ammonia on the sulphochloride, and show that this is not due to any want of homogeneity in the latter, but to the occurrence of isomeric change during the interaction.

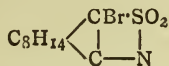
Reychler's camphorsulphonic acid is probably an *α*-acid, the sulpho-group occupying the same position as the bromine atom in *α*-bromocamphor. When the sulphochloride or sulphobromide is acted on with dilute ammonia the action proceeds normally, only the *α*-sulphonamide, m. p. 223°, being produced; the isomeric *α'*-sulphonamide, m. p. 132°, is formed when strong ammonia is used, and the action is allowed to proceed violently; it is a labile substance, and is readily converted into the stable *α*-sulphonamide by the action of bromine or of mineral acids.

Camphor-α-sulphobromide, m. p. 93°, $[\alpha]_D +26^\circ$.
Camphor-α-sulpho-p-bromoanilide, m. p. 165°, $[\alpha]_D +56^\circ$.
Camphorsulphopiperidide, m. p. 140°, $[\alpha]_D +32.2^\circ$, is the chief product of the action of piperidine on the sulphochloride, but a more soluble *piperidide*, m. p. 55°, $[\alpha]_D +33.6^\circ$, is also produced.

α-Bromocamphor-α'-sulphonic acid is readily isolated in the form of the calcium salt, $(\text{C}_{10}\text{H}_{15}\text{SO}_4)_2\text{Ca} + 6\text{H}_2\text{O}$; this crystallises from hot water in pearly scales. The *sulphochloride*, m. p. 65°, $[\alpha]_D +104^\circ$, yields a single *sulphonamide*, m. p. 156°, $[\alpha]_D +106^\circ$, which is reduced by zinc dust and acetic acid to camphor-*α*-sulphonamide. The *sulphoanilide*, m. p. 106°, $[\alpha]_D +177^\circ$ is reduced to camphor-*α*-sulphoanilide. The *sulphopiperidide*, m. p. 123°, $[\alpha]_D +111^\circ$ is reduced to the camphorsulphopiperidide, melting at 140°.

α -Chlorocamphor- α -sulphochloride has m. p. 60° , $[\alpha]_D +81^\circ$. The sulphonamide, m. p. 141° $[\alpha]_D +83^\circ$ is reduced to camphor- α -sulphonamide.

When α -bromocamphor- α -sulphonamide is boiled with acetic anhydride it is converted into an anhydride, $C_{10}H_{14}BrSO_2N$, m. p. 186° , $[\alpha]_D +98^\circ$, to which the formula—



may perhaps be assigned; it is reduced by zinc dust and acetic acid to camphor- α -sulphonamide. By the action of bromine on camphor-sulphonamide or of bromhydric acid on α -bromocamphor- α -sulphonamide, the stereoisomeric anhydride of α -bromocamphor- α -sulphonamide, m. p. 166° , $[\alpha]_D +41^\circ$, is also produced. By the further action of bromine these are converted into the anhydride, $C_{10}H_{13}Br_2SO_2N$, of a dibromocamphorsulphonamide, m. p. 195° , $[\alpha]_D -7^\circ$, which on reduction yields camphor- α -sulphonamide.

The anhydride of α -chlorocamphor- α -sulphonamide, m. p. 167° , $[\alpha]_D +60^\circ$, yields camphor- α -sulphonamide on reduction. An anhydride, $C_{10}H_{13}Cl_2SO_2N$, of a dichlorocamphorsulphonamide may be prepared by the action of chlorine on camphorsulphonamide, chlorocamphorsulphonamide, or its anhydride; m. p. 172° , $[\alpha]_D +4^\circ$, on reduction this yields camphor- α -sulphonamide.

127. "Displacement of Alkyls from Phenols by Nitration. I. Thymol." By A. T. LARTER.

Maldotti, in a recent note (*Gazetta*, 1900, xxx., II., 365), states that trinitrothymol is formed on nitrating dinitrothymol; he was unable to analyse the product, and bases his statement solely on molecular weight determinations made by the cryoscopic method. This conclusion is in opposition to the result arrived at by Armstrong and Rennie (*CHEMICAL NEWS*, 1883, xlvii., 115), who found that the so-called trinitrothymol was in reality trinitro-metacresol.

The author has repeated the experiments at Dr. Armstrong's request, and his results confirm the conclusion arrived at by Armstrong and Rennie.

The melting-point of the product from thymol is the same as that of trinitrometacresol, and is unaffected when the substance is mixed with the trinitro-compound prepared from metacresol. On methylation, the product affords an ether identical with that prepared from trinitrometacresol, the two substances melting at 91° , whether singly or in admixture, and giving the same trinitrometacresol (m. p. 136°) when subjected to the action of ammonia.

When dinitrothymol ethyl ether is subjected to nitration, it is converted into trinitrometacresol ethyl ether—an observation of importance as proving that the displacement of the alkyl does not involve the formation at an intermediate stage of a keto-compound.

128. "Taka-diastase and Reversed Ferment Action." By A. C. HILL.

The hydrolysis of dilute starch solutions by taka-diastase ends in an almost complete transformation to glucose, as shown by the combined polarimetric and copper reduction methods of estimation; no dextrin which resists further hydrolysis is formed, and there is sufficient maltase in commercial taka-diastase to convert all the maltose to glucose.

A solution containing 35 per cent of glucose and 6 per cent of maltose hydrate, that is, 41 per cent of total sugar, on treatment by taka-diastase containing maltase, was further hydrolysed until the measurements indicated nearly 39 per cent of glucose, and about 2 per cent of maltose hydrate. A 60 per cent solution of glucose, however, similarly treated, showed a reversed ferment action until its optical and reducing properties corresponded with those of a solution containing 58 per cent of glucose, and 2 per cent of maltose hydrate. On diluting the solution without boiling, hydrolysis again took place. The dif-

ference in equilibrium point in this case from that found by the author when acting on concentrated glucose solutions with yeast extract (*Trans.*, 1898, lxxiii., 634) (in the latter case the measurements at equilibrium corresponded to a mixture of 34 per cent of glucose, and 6 per cent of maltose hydrate), is probably to be explained by the presence in the yeast extract of enzymes other than maltase and diastase, whereby other polysaccharides are formed either from glucose or maltose, such ferment actions being quite distinct from a possible formation of higher polysaccharides from maltose, which may occur also in the case of taka-diastase.

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—The accurate estimation of carbon in metals by direct combustion in a stream of air or oxygen depends chiefly on the available temperature and the kind of reagent the powdered sample is mixed with. With regard to temperature one has frequently not much choice; being given a particular form of combustion furnace and a limited supply of gas. With regard to reagents we have from time to time had the following suggested:—

Powdered pumice, potass. chloride, potass. chromate, acid potass. sulphate, metallic lead, lead chromate, lead peroxide, litharge, red-lead, metallic copper, copper oxide, phosphor-copper, stannic oxide, zinc oxide, manganic oxide, and alumina.

For a particular kind of alloy each of the above may be effective, just as burning with no reagent at all may be (see *CHEMICAL NEWS*, lxxxi., 91); but with the most refractory alloy the steel-maker uses—ferrochromium—many of the above are no use whatever, except when employed at such temperatures as are generally not provided for in the laboratory.

The cheapest and perhaps most effective of the above reagents are the oxides of lead. The monoxide really ought not to be used if kept in the powdered state, because it readily absorbs both water and carbon dioxide from the atmosphere. Both the peroxide and red-lead serve very well if they can be obtained of such quality that no serious increase in weight of the KHO bulb takes place when they are ignited alone.

But unfortunately it is not easy to obtain either the peroxide or red-lead to meet this requirement, and one is therefore obliged to estimate the "blank" in as many samples as can be had and choose the best.

This is the game I have played for more than a year with red-lead, and I am now wiser by this much only:—The "blank" is generally greater in those samples which have the lighter colour, and is probably due to the carbon dioxide absorbed by that proportion of the PbO not needed to form Pb_3O_4 .

The "blank" on 10 grms. of the worse kinds of red-lead may be as much as a decigram. Ten grms. of the best kind yet met with gave a "blank" of nearly a centigram, and this was picked up casually during a visit to some paint works.*

Red-lead yielding a constant blank of 1 centigram on 10 grms. is as good in respect to impurity as many other reagents. As 6 grms. Pb_3O_4 is an ample allowance for 1 grm. of the powdered alloy, it involves a correction amounting to only 0.16 per cent carbon. A correction of this magnitude is not serious, except perhaps in the somewhat rare cases where nearly pure chromium metal, said to be free from carbon, is being examined.

In order to avoid the "blank" altogether any of the

* The firm in question have been persuaded to keep for retail sale the large cask from which the sample was taken. Their address may be had on application.

oxides of lead may be fused in the boat, and then, after cooling, the finely powdered alloy spread evenly over the surface. The reaction is naturally much less active than when the mixture is made with the dry powder, and consequently the combustion needs a longer time, and the results are somewhat uncertain.

When economy is no consideration, the sesquioxide of bismuth, made by fusing the basic nitrate in the muffle, grinding, and sieving, gives quite as good results in as satisfactory a manner as the oxides of lead do, and the fact that it can be prepared in this manner so as to yield no blank makes it a very serviceable reagent for low carbon alloys.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield.
July 4, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 24, June 17, 1901.

Researches on Chemical Equilibrium. Formation of Insoluble Phosphates by Double Decomposition. Dibasic Sodium Phosphate and Silver Nitrate.—M. Berthelot.—The total precipitation of silver in the form of phosphate during the reaction of disodium phosphate on silver nitrate takes place in the cold, only when the two salts react in molecular proportion, the phosphoric acid existing in solution under the form of the mono- and di-basic salts. The total precipitation of phosphoric acid under the form of silver phosphate only takes place when three molecules of silver nitrate to one molecule of disodic phosphate are used with the final addition of soda in sufficient proportion to neutralise the acid excess; phenylphthalein being used as an indicator. In all cases the initial mixture gives place to phenomena of equilibrium between the two acids, from which, except in the first case, the formation of a certain quantity of soluble silver phosphate results. Finally, the precipitates formed in presence of an excess of phosphate contain, in addition to the predominant di-silver phosphate, a certain quantity of di-silver and silver-sodium phosphates; that is to say, the double salts, characteristic of the final state of the system, as is the case in the great majority of phenomena of chemical equilibrium.

New Syntheses effected by means of Molecules containing the Methylene Group Associated with one or two Negative Radicles. Action of Epichlorhydrine and Epibromhydrine on Sodium Benzoyl Acetic Ethers.—A. Haller.—The author's experiments show that the molecules which contain the ethylene oxide group, such as epichlorhydrine or epibromhydrine, are added directly and in the cold, to the sodium derivatives

of the bodies containing $\text{CH}_2 \begin{smallmatrix} \nearrow \text{R} \\ \searrow \text{R}' \end{smallmatrix}$ (R and R' being the

negative radicles), and probably also to the bodies containing the complex radicle— CHNaCO —or the tautomeric complex radicle— CH=CONa . In the case where the β -ketonic ethers are used, the halogen keto-oxyacids are the first things obtained; these when liberated from their soda salts are transformed into halogen keto-actones of

R.CO.CH=CO
the form $\text{CH}_2 \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{CH}_2 \end{smallmatrix}$. These halogen keto-

actones are susceptible under the influence of alkalis of giving rise to ketone-glycols, of which up to the present time scarcely any representatives are known. On reduction these latter bodies very easily give rise to new glycerins. Under the same conditions, the keton-actones can also be decomposed into a mono-basic acid (benzoic

acid in the case considered), and an acid which can only be a glycol acid.

Thallium Chlorobromides.—V. Thomas.—The author's experiments show that (1) excess of bromine reacts on thallous chloride in presence of solvents not having any chemical action, to form the chlorobromide, $\text{Th}_3\text{Cl}_2\text{Br}_4$; (2) in presence of solvents—such as carbon disulphide, which are capable of combining with the halogens—thallous chloride is transformed into the bi-bromide, ThBr_2 . The transformation is total in presence of a sufficient quantity of bromine; (3) in the dry way, the normal addition products of thallous chloride can be obtained. In presence of excess of bromine the chlorobromide, ThClBr , is produced; (4) the apparent displacement of chlorine by bromine ought to be attributed to the formation of intermediate compounds, which are very unstable and capable of reacting with the solvent.

The Reactions of Acetylene with Cuprous Chloride Dissolved in a Neutral Solution of Potassium Chloride.—R. Chavastelon.—The action of acetylene on a saturated neutral solution of cuprous chloride in potassium chloride leads to identical results whether this solution is acid or neutral. In the case of a neutral solution, and one in which the velocity of the gaseous current is not rapid, an active agitation is necessary.

Separation of Cobalt and Nickel by the Electrolytic Method.—Dimetry Balachowsky.—The author's method of separating nickel and cobalt electrolytically consists in the use of a tenth-normal acetic solution of these two metals. To this solution are added 3 grms. of the metal, 3 grms. of ammonia sulphocyanate, 1 gm. of urea, and 1 to 2 c.c. of ammonia, in order to neutralise the excess of acetic acid. The E.M.F. should have a maximum of 1 volt, and the current 0.8 ampère, the temperature of the experiment being 70° or 80°. The time required is about an hour and a half. The nickel and sulphur will be deposited on the cathode, the cobalt remaining in solution. A little nitric acid dissolves up the nickel, and the sulphur can be separated from the dissolved nickel by filtration.

BIRKBECK INSTITUTION,

Breams Buildings, Chancery Lane, E.C.

LECTURES AND PRACTICAL WORK in—

CHEMISTRY .. J. E. MACKENZIE, Ph.D., D.Sc.

PHYSICS .. A. GRIFFITHS, D.Sc.

METALLURGY .. G. PATCHIN, A.R.S.M.

DAY CLASSES.—

CHEMISTRY—Tuesday, Thursday, Saturday, 10—1.

PHYSICS—Monday, Wednesday, Friday, 2.30—5.30.

METALLURGY—Monday, Wednesday, Friday, 10—1.

EVENING CLASSES in all subjects.—

Every Evening except Saturday, from 6 p.m.

ACETONE.

JOHS. OSWALDOWSKI,
ALTONA, near HAMBURG.

BRYAN CORCORAN LIM.

MILLSTONE BUILDERS,
WIRE WEAVERS, MACHINE MANUFACTURERS, AND
GENERAL MILL FURNISHERS.

Sole Makers of MILBURN'S
Patent Conoidal Stone Grinding Mills.
Especially suitable for certain materials, Wet or Dry.

Works and Warehouses: Back Church Lane.
Parcel Dept.: Basement of the Corn Exchange.

31, MARK LANE, LONDON.



THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2173.

ON INDUCED RADIO-ACTIVITY PRODUCED BY SALTS OF RADIUM.

By P. CURIE and A. DEBIERNE.

M. and M^{me}. CURIE have established the fact that when any substance is placed in the neighbourhood of a radiferous salt of barium, it becomes itself radio-active. This induced radio-activity persists long after the removal of the radio-active barium salt; however, it decreases with time, at first rapidly, then more and more slowly, and appears to become asymptotic towards zero. M. A. Debierne has shown that barium salts placed in intimate contact with salts of actinium, temporarily acquire part of the properties of the radiferous salts of barium, and retain this condition for several months. On the other hand, M^{me}. Curie has observed, when measuring the radio-activity of oxide of thorium, irregularities which have not yet been explained. M. Owens made the same observations, and showed that the air currents suppress, to a certain extent, a part of the activity of oxide of thorium. M. Rutherford, examining this phenomenon over again, showed that air which had been kept near oxide of thorium and then taken some distance away, retained its conducting power for about ten minutes.

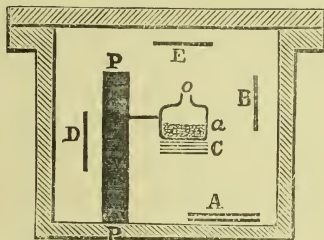


FIG. 1.

He also observed that oxide of thorium was able to produce phenomena of induced radio-activity similar to those caused by salts of radium. Finally, he observed this important fact, that bodies charged with negative electricity are more energetically active than those which are not so charged. M. Rutherford explains these phenomena by admitting that oxide of thorium gives off a particular radio-active emanation susceptible of being carried off by the air and charged with positive electricity by the positive ions in the air. This emanation should

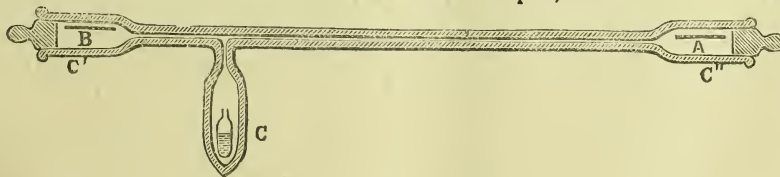


FIG. 2.

be the cause of induced radio-activity. M. Dorn has reproduced, with the radiferous salts of barium, the experiments which MM. Owens and Rutherford made with oxide of thorium. Finally, let us recall the fact that from the commencement of their researches on radio-active bodies, M. and M^{me}. Curie were able to obtain, by heating pitchblend, a gas which remained radio-active for a month. (*Comptes Rendus*, Nov., 1899).

We have undertaken a fresh lot of experiments on this induced radio-activity, which shows itself under very varied aspects, and of which the nature appears to us to be very far from elucidation.

Radio-activity has been studied by electric means. We quote the following experiments:—1. Induced radio-activity is much more intense when we operate in a closed vessel. The active matter is placed in a small bulb of thin glass, *a*, open at *o*, and placed in the middle of a completely closed vessel (Fig. 1). Various plates, *B*, *D*, *E*, suspended in different parts of the vessel, become active to about the same extent after about one day's exposure. The plate *D*, placed out of the radiating range behind the lead screen *P*, *P*, became as active at *B* and *E*. A plate such as *A*, resting on the bottom, is strongly acted on the exposed side by the air of the box; the face opposite the surface of the box is not sensibly affected. In a series of plates in contact, *C*, placed close to the bulb, it is only the outer face of the last plate exposed to the air which is strongly acted upon. Every substance appeared to be acted upon in about the same manner (lead, copper, aluminium, glass, ebonite, card, paraffin).

With very active chloride of barium (atomic weight of the metal = 174), plates exposed for several days attained an activity 8000 times greater than a plate of metallic uranium of the same dimensions. When exposed to the free air, they lose the greater part of their activity in a day. The activity disappears much more slowly when the plates are left in the closed vessel after having removed the active substance. Finally, if we repeat the above experiments with the bulb *a* completely closed, we obtain no induced activity.

2. The small chamber *c* (Fig. 2), containing the active body, communicates with the chambers *c'* and *c''*, containing the bodies *A* and *B* to be acted upon, by means of capillary tubes having an interior diameter of 0.1 m.m., and lengths of 5 c.m. and 75 c.m. The chambers *c*, *c'*, *c''*, being very small, the action took place very rapidly and as strongly as if *A* and *B* were in the same chamber as the active body.

These phenomena have been observed with various radiferous salts of barium (chloride, sulphate, carbonate). Compounds of actinium also produce induced radio-activity. On the other hand, salts of polonium, even when very active, do not produce any similar effect. As we know, further, that polonium does not emit any rays deviable by the magnetic field, it may be as well to compare these two facts one with the other.

We may conclude from these first experiments, that the radiations from radium do not take any part in the phenomena of induced radio-activity. The only radiations which could interfere would be those extremely absorbable ones which act on the air in immediate contact with the radiant matter.

Induced radio-activity is transmitted in the air through short distances, from the radiant matter to the body to be acted upon; it can also be transmitted through

capillary tubes. Bodies are acted upon progressively, the more rapidly as the vessel containing them is the smaller, and they tend towards a limit of induced activity as in the phenomenon of saturation. The limit of activity is the higher as the active body is itself the more active.

M. Rutherford's theory of emanation allows of the explanation of these different results; but, as we can

easily conceive other satisfactory explanations, it appears to be somewhat premature to adopt any particular theory just yet. Further, new facts are necessary to settle the question.

However it may be, this phenomenon appears to be one of the most important properties of radio-active bodies. Perhaps it is the necessary complement to deviable radiation.—*Comptes Rendus*, cxxii., No. 9.

THE NATURE AND ORIGIN OF THE POISON OF *LOTUS ARABICUS*.*

By WYNNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Scientific and Technical Department of the
Imperial Institute,

and
T. A. HENRY, B.Sc., *Salters' Company's Research Fellow*
in the Laboratories of the Imperial Institute.

THE authors have already given a preliminary account (*Roy. Soc. Proc.*, 1900, vol. lxxvii., p. 224), of this investigation, and have shown that the poisonous property of this Egyptian vetch is due to the prussic acid which is formed when the plant is crushed with water, owing to the hydrolytic action of an enzyme, *lotase*, on a glucoside, *lotusin*, which is broken up into hydrocyanic acid, dextrose, and lotoflavin, a yellow colouring matter.

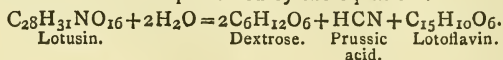
The authors have continued the investigation with the object of ascertaining the properties and chemical constitution of lotoflavin and of lotusin, and also of studying the properties of lotase in relation to those of other hydrolytic enzymes.

Lotusin.

Lotusin can be separated from an alcoholic extract of the plant by a tedious process giving a very small yield, about 0.25 per cent.

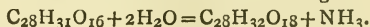
Lotusin is a yellow crystalline glucoside, more soluble in alcohol than in water. When heated it gradually decomposes without exhibiting any fixed melting-point. Combustions of specially purified material gave numbers agreeing with those deduced from the formula $C_{28}H_{31}NO_{16}$.

In the preliminary notice the formula $C_{22}H_{19}NO_{10}$ was provisionally assigned to lotusin on the assumption that one molecule of dextrose is formed by its hydrolysis. The formula given above, as the result of ultimate analysis, is confirmed by the observation that two molecules of dextrose are produced by acid hydrolysis, which is therefore represented by the equation:—

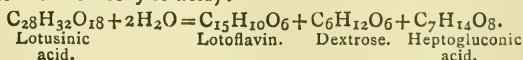


When a solution of lotusin is warmed with dilute hydrochloric acid, hydrolysis readily occurs. The liquid acquires a strong odour of hydrocyanic acid, and a yellow crystalline precipitate of lotoflavin is thrown down, whilst the solution strongly reduces Fehling's solution. Dilute sulphuric acid only very slowly effects the hydrolysis of lotusin.

When warmed with aqueous alkalis, lotusin is gradually decomposed, ammonia being evolved, and an acid formed to which the name *lotusinic acid* has been given.



Lotusinic acid is a monobasic acid furnishing yellow crystalline salts. It is readily hydrolysed by dilute acids, forming lotoflavin, dextrose, and heptogluconic acid (dextrose-carboxylic acid):—



With the exception of amygdalin, lotusin is the only glucoside definitely known which furnishes prussic acid as a decomposition product.

Lotoflavin.

Lotoflavin is a yellow crystalline colouring matter readily dissolved by alcohol or by hot glacial acetic acid, and also by aqueous alkalis forming bright yellow solutions. It is always present to some extent in the plants, especially in old plants. Ultimate analysis leads to the formula $C_{15}H_{10}O_6$. It is therefore isomeric with luteolin, the yellow colouring matter of *Reseda luteola* and with fisetin, the yellow colouring from young fustic, *Rhus cotinus*. *Morin*, from *Morus tinctoria*, appears to be hydroxylotoflavin.

Lotoflavin does not form compounds with mineral acids. It furnishes a tetracetyl derivative and two isomeric mutually convertible trimethyl ethers which are capable of forming one and the same acetyl-trimethyl-lotoflavin. By the action of fused potash lotoflavin is converted into phloroglucin and β -resorcylic acid.

Dextrose.

The sugar resulting from hydrolysis has been found to correspond in all properties with ordinary dextrose.

Hydrocyanic Acid.

The amount of prussic acid given by plants at different stages of growth has been ascertained. Mature plants bearing seed-pods have furnished 0.345 per cent of this acid, calculated on the air-dried material which corresponds with 5.23 per cent of lotusin. Younger plants bearing flower buds gave 0.25 per cent, whilst still smaller quantities were furnished by very young plants, and hardly any by quite old plants from which the seeds had fallen.

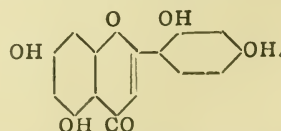
The formation of the poison therefore seems to reach its maximum at about the seeding period, and after this period to diminish rapidly. The Arabs are aware that the plant is safe to use as a fodder when the seeds are quite ripe, but not before. We have found that it is the lotusin which disappears during the ripening of the seeds. Old plants contain some lotase and lotoflavin, but little or no lotusin.

Lotase.

In its general properties lotase resembles other hydrolytic enzymes, from which, however, it differs in several important respects. It may be compared with emulsin, the enzyme of bitter almonds. Emulsin, however, only attacks lotusin very slowly, whilst lotase has but a feeble action on amygdalin, the glucoside of bitter almonds. Lotase is much more readily injured and deprived of its hydrolytic power than emulsin. On this account it is difficult to isolate in the solid state. Its power is not only rapidly abolished by heat, but is also gradually destroyed by contact with alcohol or glycerin. Besides lotase, the plant contains an amyolytic and a proteolytic enzyme.

Constitution of Lotoflavin and Lotusin.

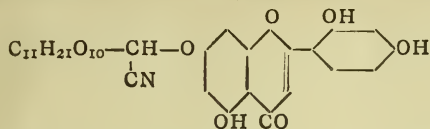
Having regard to its reactions, and especially to the production, by the action of fused alkali, of β -resorcylic acid and phloroglucin, the authors conclude that lotoflavin should be represented by the formula:—



which is that of a compound belonging to the same class, of phenylated pheno- γ -pyrones, as its isomerides luteolin and fisetin. The peculiarity shown by lotoflavin of containing four hydroxyl groups, but furnishing only a trimethyl ether, is accounted for by one of the hydroxyl groups being in the ortho position to a carbonyl group.

The reactions of lotusin are best represented by the formula:—

* Abstract of a Paper read before the Royal Society, June, 20, 1901.



which is that of a lotoflavin ether of maltose-cyanhydrin.

This formula satisfactorily accounts for the partial hydrolysis of the glucoside by alkalis giving lotusinic acid and ammonia, and for the decomposition of the substance by acids giving lotoflavin and maltose-carboxylic acid which is immediately decomposed into dextrose and heptogluconic acid. It also accounts for the hydrolysis of lotusin, by acids, into lotoflavin and maltose, which is further changed to dextrose.

In order to definitely localise the position of the cyanogen group in lotusin, the behaviour of several cyanhydrins of known constitution have been examined with reference to the question as to whether they would furnish hydrocyanic acid when acted on by dilute hydrochloric acid. It was found that mandelic nitrile, lævulose cyanhydrin, and pentacetyl gluconitrile, in which the cyanogen group is known to occupy a position similar to that assumed for it in the formula suggested for lotusin, are, like lotusin, easily decomposed by dilute hydrochloric acid forming prussic acid, and the corresponding aldehyde or ketone.

The authors wish again to express their obligations to Mr. Ernest A. Floyer, of Cairo, Member of the Egyptian Institute, who has spared neither trouble nor expense in collecting in Egypt, and despatching to this country, the material required for this investigation.

THE PHARMACOLOGY OF PSEUDACONITINE AND JAPACONITINE CONSIDERED IN RELATION TO THAT OF ACONITINE.*

By J. THEODORE CASH, M.D., F.R.S.,
Regius Professor of Materia Medica in the University of Aberdeen,

and
WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Scientific Department of the Imperial Institute.

In a previous paper on the "Pharmacology of Aconitine and some of its Principal Derivatives" (*Phil. Trans.*, 1898, vol. cxc., p. 239), we have given an account of the physiological action of this, the highly toxic alkaloid of Monkshood (*Aconitum Napellus*), and of its principal derivatives, and we have also discussed the ascertained physiological effects of these substances in relation to their chemical constitution. The results of this investigation have proved to be of much practical importance in connection with the pharmaceutical and medical employment of aconite, especially in demonstrating the partial antagonism to aconitine of benzaconine, and in a greater degree of aconine, both of which derivatives accompany the parent alkaloid in the plant and in the pharmaceutical preparations made from it, which have been hitherto used medicinally. Although it seems likely that these separate alkaloids, and especially aconine, may be useful as therapeutic agents, it is now clear that for the purpose for which aconite is employed, the pure alkaloid, aconitine, should be used in the place of the indefinite mixture of physiologically antagonistic alkaloids contained in pharmaceutical preparations made from the plant.

In a series of papers communicated to the Chemical Society, and published in the *Journal of the Chemical Society* (1891-99), one of us, in conjunction with his pupils, has described the chemical properties of the toxic alkaloid contained in two other species of alkaloid, viz., *Aconitum ferox* or Indian or Nepaul Aconite, and

Aconitum Fischeri or Japanese aconite. The medicinal employment of these potent drugs has been very restricted in the absence of any definite knowledge as to the nature of their constituents and the physiological action to which they give rise.

Aconitum ferox has long been known to botanists and travellers in India as a poisonous plant of great virulence. It is used in Indian medical practice under the vernacular name of "Bikh." There appear, however, to be several varieties of aconite passing under this vernacular name. This is a subject which we are at present investigating with the assistance of the Government of India.

In 1878 Alder Wright isolated a crystalline, highly toxic alkaloid from the root of the plant, and named it pseudoaconitine. In 1897 (*Proc. Chem. Soc.*, 1895, p. 154; *Trans. Chem. Soc.*, 1897, p. 350), one of us gave an account of a complete investigation of the chemistry of this alkaloid, the results of which have led to a modification in certain important respects of the conclusions arrived at by Wright and his co-workers. Our results have been confirmed by Freund and Niederhofheim (*Ber.*, vol. xxix., pp. 6, 852).

For details of the chemistry of pseudoaconitine and its derivatives, reference must be made to the paper already referred to (*loc. cit.*). We may here briefly record the chief properties of the alkaloid.

Pseudoaconitine is a crystalline alkaloid whose composition differs from that of aconitine, being expressed by the formula $C_{36}H_{49}NO_{12}$. The crystals melt at 202° , and are sparingly soluble in water, but readily in alcohol. The salts are usually crystalline and soluble in water. Their solution and those of the base produce in excessively minute quantities, a persistent tingling of the tongue, lips, and other surfaces with which they are placed in contact, in this respect resembling aconitine and its salts, which produce the same effect.

When heated in the dry state at its melting-point pseudoaconitine evolves a molecular proportion of acetic acid, leaving another alkaloid, pyropseudoaconitine. This alkaloid, like the corresponding pyro-derivative of aconitine, does not give rise to the characteristic tingling effects of the parent base.

When a salt of pseudoaconitine is heated in a closed tube with water, as in the case of aconitine, partial hydrolysis occurs with the loss of a molecule of acetic acid, an alkaloid, veratryl-pseudoaconine, being left. This alkaloid, like the corresponding benzaconine, derived by similar means from aconitine, produces neither the tingling sensation nor the toxic effects of the parent base.

The complete hydrolysis of pseudoaconitine, which is reached when the above mentioned veratryl-pseudoaconine is heated with alkalis, produces, instead of the benzoic acid furnished by aconitine, veratric or dimethylprotocatechuic acid, together with a base, pseudoaconine, not susceptible of further hydrolysis. Whilst there is thus a strong general resemblance in chemical constitution between pseudoaconitine and aconitine, the benzoic radical of aconitine is replaced in pseudoaconitine by the veratric radical of veratric acid, whilst there are probably also constitutional differences in the central nucleus.

The composition and properties of the toxic alkaloid present in Japanese aconite, "*Kuza-uzu*," regarded by botanists as *Aconitum japonicum* or *A. Fischeri*, has been the subject of some dispute among chemists who have examined it. Wright regarded it as chemically different from aconitine, both in composition and in structure, being an anhydro- or apo-derivative formed by the loss of water and conjugation of 2 molecules of an unknown alkaloid of the aconitine type. He assigned to it the formula $C_{66}H_{88}N_2O_{21}$. Lübke afterwards studied the properties of japaconitine, and pronounced it to be identical with aconitine, and, more recently, Freund and Beck have reached the same conclusion. Later, one of us, in conjunction with H. M. Read (*Journ. Chem. Soc.*, 1899), subjected japaconitine to a very detailed investigation, in the course of which its properties and those of its principal

* Abstract of a Paper read before the Royal Society, June 20th, 1901.

derivatives were defined and compared closely with those of aconitine. We believe that these results leave little room for doubting that japaconitine is a distinct alkaloid different from aconitine, although Wright was mistaken in the view he took of its composition and constitution. Superficially japaconitine bears a very strong resemblance to aconitine; it is, however, richer in carbon, and the physical properties of its derivatives do not agree with those of aconitine. To this alkaloid we have provisionally assigned the formula $C_{34}H_{49}NO_{11}$, and have retained for it the name of japaconitine suggested by Wright.

In general, the decomposition of japaconitine resembles that of aconitine, but the physical properties of the resulting derivatives are not the same. By the action of heat it furnishes acetic acid and jappyracnitine; on partial hydrolysis, japbenzaconine is obtained besides acetic acid; whilst on complete hydrolysis, the products are acetic acid, benzoic acid, and japaconine. Whilst therefore the constitution of the central nucleus appears to be different, both aconitine and japaconitine contain the acetyl and benzoyl groups, whilst in pseudoaconitine the acetyl and veratryl groups are present.

In the present paper the physiological action of specially purified pseudoaconitine and japaconitine are recorded and compared with aconitine.

The differences found are nearly always differences of degree and not differences of kind, a result which bears out the close constitutional relationship which is to be inferred from their chemical reactions. Although there are probably constitutional differences in the central nuclei of the three alkaloids, the same constitutional type is to be seen in each, and the substitution of a veratryl group (in pseudoaconitine) for an acetyl group (in aconitine) counts for little in influencing the characteristic physiological action.

In order to bring the action of aconitine, pseudoaconitine, and japaconitine into a contrast, which may be readily apprehended at a glance, the following summary will be useful:—

Heart.—All three alkaloids have a similar effect upon the heart of such mammals as have been observed. Pseudoaconitine is quantitatively more energetic than the other two towards cats, but is certainly not nearly twice as toxic when artificial respiration is practised. Towards the frog's heart pseudoaconitine is slightly less powerful than the other two, of which japaconitine is rather the more active.

Vagus Nerve and Inhibitory Mechanism in Heart.—Heart slowing from increased central vagus activity is produced by all these alkaloids, and similar results follow section and stimulation of the nerve at this and later stages of poisoning by one and all of them, both in mammals and frogs.

Respiration.—There is less tendency to acceleration of respiration in mammals poisoned by pseudoaconitine than when the other two alkaloids are employed; further the dyspnoeal conditions develop more suddenly and the central depression of respiration is greater. Japaconitine is at first slightly more depressant than aconitine, but thereafter the tendency to acceleration of respiration is sooner developed, otherwise the general features of their action are similar.

Blood.—All the aconitines produce a deleterious effect upon the hæmoglobin and coloured corpuscles of the blood when they are given repeatedly in large doses. As far as has been ascertained this is due to impairment in the nutrition of the animal rather than to a direct action.

Frogs kept in a watery medium or in contact with a moist surface, develop oedema after receiving any of the aconitines, but this condition is most marked and the hydræmia of the blood is more pronounced and lasting after pseudoaconitine.

Brain and Cord.—All aconitines appear to have a similar effect qualitatively on the brain and cord of rabbits, pigeons, and frogs.

Temperature.—The initial elevation of temperature often seen in rabbits which have received aconitine or

japaconitine is less frequently observed after pseudoaconitine. A slightly greater and more enduring fall of internal temperature is witnessed after the latter, when the dose is large, and bears a like relationship to the lethal amount.

Repeated Administration.—Some tolerance is established on the part of rabbits towards all the aconitines, and this is manifested with reference to temperature reduction, to the cardiac effect, and, to a lesser extent, to respiration; the general toxicity undergoing a reduction which is not, however, extensive. Less tolerance is shown towards pseudoaconitine than towards the other two; it has been found impossible hitherto to determine how far rapidity of elimination varies between the alkaloids.

Sensory Nerves.—Local applications of the aconitine ointments of equal strengths are followed by a somewhat more powerfully depressant and enduring effect when these contain aconitine or japaconitine than pseudoaconitine. This statement has reference to cutaneous sensory and thermic impressions in the human subject. The difference is at most but slight.

Motor Nerve and Muscle.—The action of the individual alkaloids is much the same whether specimens of *R. esculenta* or *R. temporaria* are used. It is more difficult to reduce reaction or to produce insensitiveness of the intramuscular motor nerves by pseudoaconitine than by the other alkaloids. The so-called curare-like action has been found for all the alkaloids to be much feeble than was at one time supposed.

Direct contact of the alkaloidal solutions with muscle-nerve preparations reduces excitability, the muscle being affected by solutions containing less than 1 in 1,000,000, and the nerve by solutions still weaker. Pseudoaconitine is recognised as producing a rather weaker effect than the two other alkaloids, which are nearly equal to one another, japaconitine being slightly the more energetic.

The results of the experiments detailed in this paper do not in all respects agree with previous observations; especially is this the case with regard to the relative toxicities of the three aconitines. The general order of toxicity towards mammals is pseudoaconitine, japaconitine, and aconitine, which is the least toxic. Pseudoaconitine has been found (roughly speaking) twice as toxic as aconitine towards the small mammals and birds used in the research. This agrees closely with the results of Adelheim (*Forens. Chem. Untersuch.*, Dorpat, 1860), and Böhm and Ewers (*Arch. f. Exp. Path. u. Pharm.*, 1873, Bd. 1, s. 385). Cloetta (*Lehrb. d. Arzneim. u. Arzneiverordnungn.*, Freib., 1885), states that pseudoaconitine is the stronger alkaloid, but gives no proportion. Our results differ from those of Nothnagel and Rossbach (*Mat. Med. u. Therap.*, Fr., 1880, 685), who state that pseudoaconitine is seventeen times as active as aconitine, and of Harnack and Meunicke (*Berl. Klin. Wchschr.*, 1883, No. 43, s. 657), who find the under margin of active dosage equal. Kobert (*Lehrb. d. Intox.*, s. 657), finds pseudoaconitine and aconitine to be in activity "ziemlich gleich."

The relative toxicity of japaconitine to aconitine is approximately as ten to about nine towards the small mammals and birds which were used. Previously, japaconitine has been seldom contrasted with the other two aconitines, but has been recognised as stronger than aconitine by Langaard (*Arch. f. Path. Anat.*, 1880, lxxix., s. 229), and in one series of observations by Harnack and Meunicke. Kobert, on the other hand, does not separate japaconitine from aconitine and pseudoaconitine in toxicity.

Dosage.—Based upon the observations made, the relative doses for therapeutical purposes would be approximately, regarding that for aconitine as the unit, for pseudoaconitine 0.4 to 0.45, and for japaconitine 0.8.

Towards frogs the toxicity of these alkaloids is by no means so great (per grm. body-weight), as it is towards the same unit of the mammals and birds included in this research. Thus the lethal dose per kilo. mammalian weight may only be lethal to 140 to 170 grms. of frog weight, or even to less, according to the time of year. A medium-sized rabbit may therefore be poisoned by a dose

of aconitine or japaconitine which would suffice to destroy six or eight frogs.

Japaconitine is slightly more toxic towards both mammals and frogs than is aconitine, but the higher toxicity of pseudaconitine towards birds and mammals is not associated with an equal activity towards frogs, for it exerts towards both *R. esculenta* and *R. temporaria* a slightly lower toxicity than do either of the other alkaloids.

There is no essential difference in the reaction of *R. esculenta* and *R. temporaria* respectively to individual aconitines beyond a greater or less accentuation of one or other symptom, as for example more excited movement in the latter, more reduction of reflex in the former, but in all parallel series of observations the resistance of *R. esculenta* has proved to be slightly greater to all the aconitines examined.

As concerns the local action of the aconitines upon sensory (cutaneous) structures in man, the differences are so trifling as to be negligible.

As regards the therapeutical employment of aconitine, japaconitine, and pseudaconitine, the great similarity in their physiological actions, amounting almost to a qualitative identity which is established by this investigation, justifies the employment of any one for internal administration, provided that the dosage is properly regulated. Given in the just proportions mentioned above, the three alkaloids would exert the same action. We strongly recommend the use of a pure alkaloidal salt in preference to preparations made from the plants, since the latter would be difficult to standardise, and even if this were done, the action of the aconitines would be modified to a greater or less extent by the other alkaloids present in the vegetable preparation.

For local applications the three alkaloids may be introduced into ointments in identical proportions. The greater toxicity of pseudaconitine need not prevent its use in this department of treatment if it is remembered that all applications of the aconitines, externally, are to be considered dangerous if any abrasion of the skin is present.

The chemical part of this inquiry has been conducted in the Laboratories of the Scientific Department of the Imperial Institute, with the assistance and co-operation of the Government of India. Our thanks are specially due to Dr. George Watt, C.I.E., Reporter on the Economic Products to the Government of India, for the interest he has shown in the investigation, and for the care he has taken in the collection of the necessary material.

The physiological experiments have been conducted in the Department of Materia Medica and Pharmacology of the University of Aberdeen, and have been assisted by a grant made by the Royal Society from the Government Fund. The assistance of Drs. Esslemont and Fraser has been very valuable in carrying out some of the observations entailed in this department of the research.

"MOHAWKITE."

By JOSEPH W. RICHARDS.

DR. KÖNIG has given the name Mohawkite to the nickelliferous and cobaltiferous variety of domeykite found at the Mohawk mine. He bases this on his analyses, corresponding to $(\text{Cu}, \text{Ni}, \text{Co})_3\text{As}$ (*Am. Journ. Sci.*, December, 1900; *Zeit. für Krystallographie und Mineralogie*, 1901, xxiv., 70).

Dr. Ledoux published the results of an analysis of a mineral from the same mine (*Engineering and Mining Journal*, April 7, 1900), which corresponded closely to $(\text{Cu}, \text{Ni}, \text{Co})_4\text{As}$, and which he proposed should be called Mohawkite. Dr. König, however, throws doubt upon the formula obtained by Ledoux; also claims that if Cu_4As does exist, a new name must be found for it, as he has pre-empted the name Mohawkite for his variety of domey-

kite. The object of this communication is to substantiate Ledoux's analysis and formula, and thereby prove the existence of the new species $(\text{Cu}, \text{Ni}, \text{Co})_4\text{As}$.

Last autumn the writer received from Foote, of Philadelphia, a specimen from the Mohawk mine marked "Mohawkite?" Analysis of the material, completely freed from gangue, gave—

	Per cent.
Copper	70.8
Cobalt	6.4
Nickel	trace
Iron	0.0
Arsenic (by difference) ..	22.8

100.0

The atomic ratios from the above are—

Copper	$\frac{70.8}{63.4} = 1.117$	} 1.225
Cobalt	$\frac{6.4}{59} = 0.108$	
Arsenic	$\frac{22.8}{75} = 0.304$	

Hence, the atomic ratio $\frac{1.225}{0.304} = 4.003$ and the formula

$(\text{Cu}, \text{Co}, \text{Ni})_4\text{As}$.

Dr. Ledoux's analysis, as calculated by König, gives the corresponding atomic ratio $\frac{1.228}{0.302} = 4.066$. König, however, makes a slight mistake in adding the basic valencies, and the correspondence is still closer. I have re-calculated Ledoux's results, as follows:—

	Atomic ratios.
Copper	68.6
Cobalt	1.2
Nickel	6.55
Iron	0.23
Sulphur	0.53
Arsenic	22.67
	100.0

Assuming the sulphur to be present as RS, we subtract its ratio 0.017 from that of the bases, and there remains

$\frac{1.201}{0.302} = 3.98$. Ledoux's ratio is therefore

I would propose the name *Ledouxite* for the compound Cu_4As , the existence of which no longer appears doubtful. It carries small percentages of cobalt and nickel and is similar in appearance to algodonite, with density 7.8 (Ledoux) or 8.07 (Richards). The latter was taken on clean material free from gangue.—*American Journal of Science*, xi., p. 457.

EXPERIMENTS ON CHALCOPYRITE.*

By LEONARD P. MORGAN and EDGAR F. SMITH.

AT various times experiments have been made in this laboratory looking to the determination of the constitution of certain natural chemical products. Thus, the state of oxidation of the iron in pyrite, marcasite, and arsenopyrite has received considerable attention, and in the present communication it is desired to give the results of similar experiments made upon the mineral chalcopyrite. Weighed portions of the latter were exposed in porcelain boats to the action of dry hydrochloric acid gas. As the mode of procedure has been sufficiently detailed in former papers, it may be omitted here. It will suffice to note that the heat was obtained from a single Bunsen burner with a wing top. The period of heating covered one hour, beginning of course with a gentle heat, and increasing finally to a full red heat. The boat and contents

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xliii., No. 2.

were allowed to cool in the gas. On their withdrawal from the tube they were placed in a beaker containing distilled water. The combustion tube was also washed out carefully with water. The aqueous solution of the iron salt was strongly diluted, acidified with sulphuric acid, and the liquid titrated with potassium permanganate.

Results.		
Chalcopyrite, Grm.	Iron found, Grm.	Iron found, Per cent.
1. 0'2112	0'06489	30'72
2. 0'2039	0'06231	30'56
3. 0'2007	0'06164	30'70
4. 0'1996	0'06128	30'67
5. 0 2089	0'06398	30'63
6. 0'2140	0'06553	30'62

In several instances the liquid in the receiver placed at one end of the combustion tube showed traces of ferric iron when the thiocyanate test was applied. This might readily occur when it is remembered that the quantity of ferrous chloride thus volatilised was exceedingly small, and that its exposure during the time required for the completion of the experiment would be enough to cause its oxidation. However, the quantity of ferric iron was extremely small.

The formula generally assigned the mineral is CuFeS_2 , which would require 30.5 per cent of iron. The results given above therefore indicate a complete decomposition of the material by hydrochloric acid, and also show that all of the iron is in the ferrous state. This proved to be the case with marcasite. As hydrochloric acid gas does sometimes act as a reducing agent, there was a possibility that perhaps it might have transformed any ferric iron present in the mineral into the ferrous condition. To render the results as certain as possible, portions of the mineral were carefully heated in sealed tubes with a solution of copper sulphate, as had been done with marcasite. The evidence gathered in this way corroborated the first experience, and it can safely be asserted that chalcopyrite contains all of its iron in the ferrous form, and that the mineral is, perhaps, nothing more than a substituted marcasite, in which copper has replaced its equivalent of iron.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The deficiency of rain has been still further accentuated during the past month; the actual rainfall at Oxford was 1.52 inches, of which half, *i.e.*, 0.75 inch, fell on the 30th. The average fall for June during the past thirty-five years is 2.10 inches; this leaves a deficit of 0.58 inch, and brings the total deficit for the year to 2.30 inches, or 2.12 per cent.

Our bacteriological examinations of 516 samples have given the results recorded in the following table; we have also examined 57 other samples, from special stand-pipes, &c., making a total of 573 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	204
New River, filtered (mean of 125 samples) ..	8
Thames, unfiltered (mean of 25 samples) ..	1371
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 279 samples) ..	26
Ditto ditto highest	260
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	488
River Lea, from the East London Company's clear-water wells (mean of 37 samples) ..	56

Of the 441 samples of impounded and filtered water supplied to London, examined bacteriologically during the past month, thirty-six samples, or 8.1 per cent, were sterile. Ten samples out of the total number examined contained more than 150 microbes, and twenty-six samples, or 5.8 per cent, contained more than 100 microbes per c.c. The mean of the microbes in the excess samples was 155, against a corresponding mean last month of 147, showing that the quality of the water remains substantially the same as it was in the month of May.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

INTRODUCTION. (Nitration of Cellulose, Methods of Determination). A. Influence of Water on the progress of Nitration. B. Influence of Sulphuric Acid on the progress of Nitration. C. The highest attainable degree of Nitration of Cellulose by means of Nitro-sulphuric Acid. D. The solubility of Nitrocellulose in Ether-alcohol. E. Formula of Kisniemsky. F. Influence of the amount of Nitrous Acid contained in the Nitric Acid upon the percentage of Nitrogen, and the gain of Nitrocellulose. G. Influence of Nitrous Acid contained in the Nitric Acid upon the stability of Gun-cotton. H. Influence of Nitration with a higher proportion of Water upon the stability of Gun-cotton. I. Relative behaviour of different kinds of Cotton on Nitration, specially with regard to the production of Collodion-cotton. K. Examination of marketable varieties of Collodion-cotton ("soluble" Nitrocellulose for Explosive Gelatin and Art Silk. L. The behaviour of Nitrocellulose in Polarised Light. M. Colouration of Nitrocelluloses with Iodine.

INTRODUCTION.

Stages of Nitration of Cellulose.—As the molecular weight of cellulose is not known, the number of theoretically possible stages of nitration must be left undecided. Conversely, attempts have been made to establish the

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

molecular weight of cellulose from the nitrocelluloses actually prepared. If this could not supply an absolute value, yet at least it afforded a fundamental value for the cellulose formula.

Eder was able to prepare four different stages of nitration from the maximum, which formerly was said to be "trinitrocellulose," as far as "mononitrocellulose," and he therefore doubled the formerly accepted cellulose formula, $C_6H_{10}O_5$ to $C_{12}H_{20}O_{10}$.

Vieille obtained, between the same limits, eight different stages of nitration, which he described as tetra- to endeca-nitrocellulose. The "hexa-nitrocellulose" of Eder, which he would name "dodecanitrocellulose," he was unable to obtain, but only a stage of nitration lying between hexa- and penta-; a further reason for him to assign to cellulose the formula $C_{24}H_{40}O_{20}$.

Mendeleeff succeeded in preparing a nitrocellulose with 12.44 per cent nitrogen, soluble in ether-alcohol. This stands midway between the deca-nitrocellulose, shown by Vieille to be insoluble, and the soluble ennea-nitrocellulose, and is considered by him as a distinct compound. But such a half-way stage between the ninefold and tenfold nitrated cellulose is excluded by the formula $C_{24}H_{40}O_{20}$. Mendeleeff, therefore, doubled the formula again, and traced back the stages of nitration from $C_{48}H_{80}O_{40}$.

It appeared in the course of this research that a soluble form of the deca-nitrocellulose also exists; hence, from the solubility alone of Mendeleeff's product no reason can be deduced for establishing the last named formula.

It is true that $C_{24}H_{40}O_{20}$ certainly does not correspond to the actual size of the cellulose molecule, but as nothing certain is known concerning the latter, and the formula $C_{24}H_{40}O_{20}$ suffices to characterise the hitherto known stages of nitration, it might be advisable for reasons of simplicity to retain this formula provisionally. These and other reasons to be mentioned later inclined us to retain Vieille's classification and nomenclature. Unless specially mentioned, therefore, the nitration stages of the following always depend upon the formula $C_{24}H_{40}O_{20}$. The French chemists give the results of the nitrogen determination regularly in c.c. of nitric oxide reduced at 0° and 760 m.m., which are evolved from 1 grm. of the substance; while in Germany and England the proportion of nitrogen is mostly expressed in percentages. Hence a comparison of both designations is given in the following table:—

Name.	Formula.	C.c. NO from 1 grm.	Percentage N.
<i>Nitrocellulose</i> —			
Dodeca- ..	$C_{24}H_{28}O_8(NO_3)_{12}$	226.27	14.14
Hendeca- ..	$C_{24}H_{29}O_9(NO_3)_{11}$	215.17	13.47
Deca- ..	$C_{24}H_{30}O_{10}(NO_3)_{10}$	203.35	12.75
Ennea- ..	$C_{24}H_{31}O_{11}(NO_3)_9$	190.75	11.96
Octo- ..	$C_{24}H_{32}O_{12}(NO_3)_8$	177.19	11.11
Hepta- ..	$C_{24}H_{33}O_{13}(NO_3)_7$	162.36	10.18
Hexa- ..	$C_{24}H_{34}O_{14}(NO_3)_6$	145.93	9.15
Penta- ..	$C_{24}H_{35}O_{15}(NO_3)_5$	127.91	8.02
Tetra- ..	$C_{24}H_{36}O_{16}(NO_3)_4$	107.81	6.76

The nitration stages from tetra- to deca-nitrocellulose can be obtained by means of nitric acid alone; to obtain a higher proportion of nitrogen mixtures of nitric and sulphuric acids are necessary. For the production of nitrocelluloses on a large scale, mixtures of both acids are used for all the stages of nitration; therefore this method of nitration has been used almost exclusively in the present work.

We have subjected the most important factors which come into play during the process of nitration to a more exact examination, and in connection with this have confirmed the conditions which are necessary for the production of the different stages of nitration. We naturally cannot tell whether much in the information here given is not already known, and does not come into the consideration of those not initiated into such secrets of manufacture.

A few extra methods of determination may next be added.

Determination of the Nitrogen.—For this purpose the products were dried in the apparatus described by Lunge and Weintraub. The drying was then conducted at a temperature of 40°; but since, according to our observation, a slight decomposition of the sulphuric acid usually takes place at 40°, we endeavoured to avoid even this trace of decomposition, although it might not affect the results. Nothing of the kind was ever noticed at 30–32°, and it was therefore always dried at this temperature.

The nitrogen determinations were carried out in the Lunge nitrometer. The decomposition of the nitrocellulose in concentrated sulphuric acid could in most cases be carried out in the funnel of the decomposition vessel itself, only with a few short fibred products this was performed in special weighing glasses. The time of decomposition is also dependent on the physical activity of the material. As long as the structure of the cellulose is preserved, only a short time is usually necessary for complete solution. On the contrary, compact products, which offer little surface to the sulphuric acid, may require as much as twenty hours. But the use of the swan-neck funnel, used long ago by Lunge for this purpose, excludes every possibility of loss. Concentrated or slightly diluted sulphuric acid may be used for cleaning out the funnel. According to Williams the use of the latter makes the results about 0.2 per cent higher. He traces this to the rise of temperature caused by the mixture of the diluted with the concentrated sulphuric acid, and concludes that without this, *i.e.*, by using concentrated sulphuric acid alone, the decomposition is incomplete. We were not able to confirm this. Comparative analyses showed the same results by using concentrated as by using diluted sulphuric acid.

Also, after treating with concentrated acid alone, the residue, after the evolution and absorption of nitric oxide, upon further treatment with diluted acid, gave no more evolution of gas, which must be the case if Williams's assumption were correct.

The results obtained by the comparison just mentioned are here added because they afford a proof of the great accuracy of this method. All our determinations vary seldom more than 0.3 c.m. per 1 grm., *i.e.*, about 2/100.

Washing out with—	C.c. NO per 1 grm.	Percentage N.	Mean.
Concentrated sulphuric acid. . .	$\left\{ \begin{array}{l} 212.15 \\ 211.78 \end{array} \right.$	$\left\{ \begin{array}{l} 13.302 \\ 13.278 \end{array} \right.$	13.290
Diluted acid . . .	$\left\{ \begin{array}{l} 211.70 \\ 211.98 \end{array} \right.$	$\left\{ \begin{array}{l} 13.273 \\ 13.291 \end{array} \right.$	
			13.382

Determination of the Solubility in Ether-alcohol.—Two methods are in use for this determination. In the one the product is treated for some time with ether-alcohol, the insoluble portion filtered off, washed, dried, and weighed. But in this manner accurate results can only be obtained when only a small proportion of soluble material is present. Otherwise the collodion solution is difficult to filter, and in consequence a thorough washing of the insoluble part is impossible.

In these cases the other method (the so called English prescription) must be used. In this the nitrocellulose is treated with a certain quantity of ether-alcohol in closed cylinders. After the insoluble portion has settled, an aliquot part of the clear liquid above is drawn off in a pipette, evaporated, and dried at 50° till the weight is constant. The collodion thus separates out as an adhesive mass, which is with difficulty completely freed from ether-alcohol. In consequence of this the results obtained are too high. With completely soluble products 102–103 per cent was generally found. An attempt was therefore made to separate the nitrocellulose in a finely divided flocculent form; this was attained by adding water before evaporating, and stirring well till there was a permanent milkiness. In this way accurate results were obtained.

(To be continued).

AN IMPROVED METHOD OF PRODUCING
ULTRA-VIOLET SENSITIVE PLATES.*

By V. SCHUMANN.

It is a known fact that the sensitiveness and intensity of the gelatin dry plate decrease considerably from the wavelength $220\text{ }\mu$ towards the shorter waves. I have already demonstrated that the cause of this decrease lies in the insufficiency of transparency of the gelatin. Silver bromide itself gives rise to no such decrease of sensitiveness, nor does this happen when working with very small quantities of gelatin.

Upon this fact was based my former method of producing ultra-violet sensitive plates, which enabled me to investigate the rays beyond $185\text{ }\mu$. This method had its drawbacks, as I did not fail to point out at the time. I have been occupied till quite recently in obviating these drawbacks.

In this manner I have gradually obtained a plate which essentially supersedes the original in purity, in reliability, and in delicacy of gradation in the intensity. With this plate I am now carrying out my observations of the spectrum *in vacuo*, with growing success.

In its fundamental features the improved method may be represented as follows:—A silver bromide gelatin emulsion very rich in silver is prepared, allowed to stiffen, washed, and dissolved in much water, then filtered and poured upon flat glass plates, upon which the silver bromide is deposited. Half-an-hour afterwards the emulsion is poured off again. The fine film of silver bromide which remains on the plate dries, on account of its thinness, in a very short time. Immediately after drying the plate can be used for photographic purposes.

Still better results are obtained if the heavier particles of silver bromide are removed from the emulsion before filtering. The formation of the film requires in this case several hours.

Preparation of the Emulsion.—In detail the method is as follows:—9 grms. potassium bromide, 4.5 grms. gelatin (Nelson I.), and 60 c.c. distilled water are placed in a beaker of about $\frac{1}{2}$ litre capacity; further, 11.25 grms. silver nitrate and 60 c.c. distilled water in a boiling flask of $\frac{1}{2}$ litre capacity; and 20 to 30 minutes later, after which time the gelatin is sufficiently swollen, both are placed in a water-bath at 50 to 60° C., in which they remain until the melting of the gelatin is complete.

Then, using the brown, or red dark-room light, the silver solution is passed in a thin stream, or in small portions, into the gelatin solution, continuously shaken, and, after closing the beaker, its contents are vigorously shaken.

The vessel is now placed for half an hour in a water-bath of 60° C., after which its contents are carefully poured out into a porcelain basin, so that the deposit of silver bromide remains behind as far as possible. The basin is placed in the cold (not above 4° C.), or upon ice, when the emulsion is sufficiently stiffened in two to three hours. The firmer the emulsion becomes the more easily it is broken up, this being a necessary prelude to the washing.

The emulsion, cut up into small pieces with a horn spatula, is heaped up in the middle of a piece of muslin, which is then fastened together into a bag. The bag is allowed to hang for two or three hours in running water, or, if this is not convenient, in a deep glass holding at least 2 litres, which is filled with water not above 14° C. After changing the water ten times at intervals of a quarter of an hour, the dissolved salts (KBr.KNO_3), whose removal is to be effected, are washed out. The bag is now taken out of the bath, lightly pressed to remove the water adhering to the gelatin, and then hung in a glass beaker of $1\frac{1}{2}$ litre capacity, which contains 950 c.c. freshly boiled out water, cooled down to 55° C. The emulsion dissolves in it in a few minutes. It is gently stirred with

a glass rod, and then twice filtered through glass-wool (which is firmly plugged 1 c.m. deep in the tube of the funnel), into a clean beaker. The layer of wool must be of such a thickness that the emulsion only runs through slowly. The formation of bubbles must here be avoided more carefully than before by stirring with the glass rod. This is best assured by allowing the emulsion to flow from the mouth of the funnel down the side of the flask in a constant stream.

After filtering, the emulsion is immediately poured upon the glass plates, which will be presently described.

It has been shown that plates of this kind are liable to surface faults, which are apparent before development as streaks and numerous dark spots, and which develop simultaneously with the picture on plates that have been kept for some time before usage. In cases where these spots are objectionable it is best to remove from the emulsion the coarser of the silver bromide particles which it always contains in varying sizes. This can be done by pouring out the dissolved emulsion before it is filtered, into a basin with a flat bottom, and allowing it to stand for three quarters of an hour. In this manner the heavier silver bromide, which seems to favour the formation of spots, is deposited, and fine particles, which yield purer and more reliable films, remain behind in the liquid. But the deposition in the basin only answers its purpose when the layer of liquid for the stated time of deposition is correspondingly thin. I obtained the best results from a layer 4 to 5 m.m. thick.

Preparation of the Glass Plates.—The glass plates require a different preparation from ordinary photographic plates, if they are to hold, without danger of spilling, the unusually large quantity of very liquid emulsion required for the formation of the sensitive film. If one desired to use the ordinary photographic glass plate, the emulsion would overflow before it had been poured on in any quantity. This does not happen if the sharp edges of the plate are ground away. This is most easily done by means of coarse particles of emery—emery paper is less well-adapted for the purpose—which are laid upon, or firmly fastened to, a smooth foundation. The glass plate, inclined (30°) to the emery surface, is scraped upon this until a rough face of about $\frac{1}{2}$ m.m. breadth is uniformly produced in place of the sharp edge. This breadth is immaterial; the principal point is, that the sharp edge of the plate shall be everywhere converted into a rough surface, otherwise the untouched parts give an easy outlet for the overflow of the emulsion.

After this the plates are dipped for an hour or longer in nitric acid, washed with water, dried with a clean cloth, polished, and dusted. It is advisable to polish shortly before covering the plates. If a longer time elapses between the two operations, the emulsion flows less well, as the plates very readily re-absorb gases.

Before covering, the plates are laid side by side at a distance of from 1 to 2 c.m., upon a long, narrow, level plate of mirror glass, which stands on feet about 8–10 c.m. high. For convenience later, when the emulsion is to be poured on, it is advisable to let the plates project on the side of the operator with their long side 2 to 3 cm. over the edge of the mirror.

(To be continued).

Vacancies.—Applications are invited for the following Appointments:—Lecturer in Chemistry at the Borough of Swansea Municipal Technical College; salary £200–250. Assistant Lecturer and Demonstrator in Agricultural Chemistry at the University College of North Wales, Bangor; salary £120.

The Dialcylamidobenzylbenzoic Acids. Derivatives of the Benzoylised Acids.—A. Haller and A. Guyot.—The authors describe the preparation and properties of dimethylamidobenzylbenzoic acid, diethylamidobenzylbenzoic acid, ethylbenzylamidobenzylbenzoic acid, dimethylamidomethoxybenzylbenzoic acid, diethylamidomethoxybenzylbenzoic acid.—*Bull. Soc. Ch.*, No. 4.

* *Annalen der Physik*, 1901, vol. v.

AMMONIUM AMALGAM.

COEHN (*Ztschr. Anorg. Chem.*, xxv., 430) has recently, published the results of an investigation on this subject, and these are given here in abstract. The increase in volume which takes place during the formation of ammonium amalgam has been used as an argument in favour of the view that ammonia and hydrogen are absorbed as such by the mercury, and that a distinct substance, ammonium, is not in combination with the mercury. In opposition to this view it has been shown that the volumes of the gases evolved bear to each other the ratio $\text{NH}_3 : \text{H} = 2 : 1$; and further, that neither ammonia nor hydrogen is absorbed by mercury.

An attempt has been made by Landolt to obtain some experimental evidence of the metallic nature of the substance ammonium, contained in the amalgam, by bringing the freshly prepared amalgam into solutions of salts of the heavy metals and determining whether, under these conditions, ammonium can replace these metals from their salts. Treated in this manner, neither copper, nor silver, nor iron, could be precipitated. This, he says, is opposed to the view that ammonium has a metallic nature.

Le Blanc thought it possible that the ammonium might be so unstable that it would not have the power to replace metals, but would decompose into ammonia and hydrogen as soon as liberated from the amalgam.

He attempted to solve the problem as to the nature of the substance contained in the amalgam by electrolysis solutions of ammonium salts, using a mercury cathode, and comparing the polarisation on the one hand with that which results when an alkali amalgam is formed in this way, and, on the other, with that which is obtained when hydrogen alone is developed on the cathode. If the value found approximates that obtained by electrolysis an alkali salt it would argue in favour of the existence of ammonium in the amalgam. If, on the contrary, it approached the value when hydrogen alone is developed on the cathode, it would argue against the existence of ammonium. His results pointed to the existence of ammonium in the amalgam.

It has been shown that in addition to the tension at which the development of hydrogen takes place in a reversible manner, as in platinised platinum, there is a characteristic tension for each metal. Thus, the reversible evolution of hydrogen, obtained by discharge of hydrogen on a mercury cathode with continuous current, took place at 15.2 volts. If an alkali metal is in solution, using the mercury cathode, there is obtained in addition to the point at 15.2 volts another point beneath this, which changes with the nature of the alkali metal, and is, therefore, characteristic of the latter, and corresponds to the formation of the amalgam. This took place with ammonium at 1.24 volts, and is therefore completely analogous to the case of the alkali metals.

The only argument against the metallic nature of ammonium still remaining was that of Landolt, and it is this which Coehn has tested in a different manner and under different conditions. The ammonium amalgam was freshly prepared by electrolysis and dropped into a solution containing copper sulphate. A platinum wire which was connected through a galvanometer with a platinum plate suspended in the solution projected upward through the bottom of the vessel. The amalgam came in contact with the platinum point, and the action of the element, if copper is replaced, would be to deposit copper on the plate, with the simultaneous passage of a current through the galvanometer. It was found that no copper was deposited, and only a weak current of momentary duration passed through the galvanometer. To test whether Le Blanc was correct in supposing that ammonium was too unstable to replace other metals, he prepared the amalgam so that it would be more stable by electrolysis of ammonium salts, cooled down nearly to 0°.

It was found that the amalgam thus prepared did not show the tendency to swell up unless it was warmed, and it has quite a metallic appearance. When ammonium amalgam, thus prepared, was brought into a solution of copper sulphate, cooled to about the same temperature, the formation of copper amalgam could be seen with the naked eye. Observing these precautions and using the apparatus mentioned above, separation of copper on the plate took place at once.

That the replacement is not due to the hydrogen developed by the decomposition of the ammonium is shown by the fact that metals like cadmium, and especially zinc, which are not reduced by hydrogen, can be precipitated in this way from solutions of their salts.

The author has thus removed the last experimental evidence against the metallic nature of ammonium.—*American Chemical Journal*, xxv., No. 5.

THE DENSITY AND MOLECULAR WEIGHT OF OZONE.

SINCE Soret's (*Liebigs Ann. Chem.*, cxxxviii., 145; and Suppl., V., 148) celebrated work on the density and molecular weight of ozone, carried out more than thirty years ago, no work has been done on this subject until Ladenburg (*Ber. d. Chem. Ges.*, xxxi., 2508) took it up in 1898. Soret worked with a mixture of ozone and oxygen containing only 5 per cent. of ozone, and hence Ladenburg deemed it important to re-determine these values, using purer ozone.

The ozone which he used was generated in a Siemens ozoniser, whereby a mixture of ozone and oxygen was obtained containing 8 to 9 per cent. of the former, which could be easily liquefied in liquid air. The author liquefied such a mixture by means of liquid air, and then allowed the mixture to boil until most of the oxygen had boiled off. A new mixture of liquid ozone and oxygen was added to the residue, and again the oxygen was allowed to boil off. By repeating this operation several times he succeeded in obtaining 2 to 3 c.c. of a blackish-blue, non-transparent liquid. He determined the density of the gas obtained when this liquid was vaporised and also the percentage of ozone in it. The density was determined by measuring the time of escape of the gas from a Schilling's apparatus and comparing it with the time of escape of pure oxygen from the same apparatus. The apparatus had been previously tested with pure oxygen and nitrogen, and was found to give very satisfactory results.

Ladenburg thus found that the gas under investigation required 430 seconds to escape, while pure oxygen required 367 and four-tenths seconds. Hence, the density of the gas was 1.3698, that of oxygen being 1. The percentage of ozone in the gas was determined by titrating, the iodine liberated from a solution of potassium iodide by a known volume of the gas. It was thus found that the gas contained 86.16 per cent. by weight of ozone. From these data the density of pure ozone was calculated to be 1.456, that of oxygen being 1, while theoretically it should be 1.5.

Soon after the publication of these results Ladenburg (*Ber.*, xxxi., 2830) published a note in which he made a correction. In the calculations by which the above results were obtained, he really assumed the molecular weight of ozone to be 48, while this is what he was trying to prove. So he deduced two algebraic equations, which, when solved, gave him 84.4 per cent. by weight as the percentage of ozone in his mixture of ozone and oxygen, and 1.469 as the density of pure ozone.

Shortly after this Staedel (*Ber.*, xxxi., 3143) and Gröger (*Ber.*, xxxi., 3174) published, at about the same time, criticisms of Ladenburg's work, in which their chief objection was that it is impossible to calculate the density of pure ozone when the density of a mixture of oxygen

and ozone and the amount of iodine liberated from potassium iodide only are known. Staedel claimed that Ladenburg assumed ozone to be O_3 , and that in one of his equations he assumed the action of ozone on potassium iodide to consist in one atom of the oxygen in ozone liberating two atoms of iodine from the potassium iodide, an assumption which he had no right to make, since he was trying to determine whether ozone is O_3 . Gröger expressed the belief that it would be possible to determine the density of ozone only when some absorbent was used which would absorb the ozone entirely without leaving behind a volume of oxygen equal to the volume of ozone started with.

In answering these two criticisms Ladenburg (*Ber.*, xxxii., 221) agreed with Staedel and Gröger that the molecular weight of ozone cannot be determined from the density of a mixture of ozone and oxygen and the amount of iodine liberated by such a mixture, but he did not agree that this fact detracted from the value of his results.

He again called attention to the fact that the ozone prepared by him was nearly pure. After the oxygen had boiled off at -186° from the liquid mixture of ozone and oxygen, the thermometer rose 60° without any gas being evolved. The determination of the density of his ozone, which contained a little oxygen, gave the value 1.3698, which corresponds to a molecular weight of 43.8. This showed conclusively, Ladenburg thought, that the molecule of ozone is O_3 . If, for instance, it were O_4 , there would be an error in his results of over 50 per cent., and the conclusion would follow that his ozone contained 60 per cent of oxygen, for which there was not the slightest evidence.

The determination of iodine liberated from potassium iodide was made merely to ascertain the percentage of ozone in his mixture, which was found to be 84.4 per cent. This value was then used in correcting the density found to that of pure ozone and 1.469 was the result obtained, which corresponds to a molecular weight of 47.

Quite recently Brunck (*Ber.*, xxxiii., 1832), in an article on the quantitative determination of ozone, referred again to the apparently inadequate proof of Ladenburg that ozone has the molecular weight 48. This reference called forth another reply from Ladenburg (*Ber.*, xxxiii., 2282), in which he used substantially the same argument which he used against Staedel and Gröger, and further he criticises some of the results of Brunck regarding the liberation of iodine from potassium iodide in acid solution. Brunck (*Ber.*, xxxiii., 2999) answered these criticisms in a later paper.—*American Chemical Journal*, xxv., No. 5.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 19).

Determination of Chromite: Absence of Diamond.

6. The same residue was treated finally with hydrofluoric and sulphuric acids. The insoluble material was transferred to a watch-glass, and microscopically examined; as it was entirely opaque and of metallic lustre, no diamond could be present; after ignition it weighed 0.0035 grm., and gave the reactions of chromium. The above number corresponds to 0.35 per cent of chromite in the unattracted material; but it is only a minimum, for part of the chromite, being very finely divided, would pro-

bably yield to the attack of the acid, and be carried into solution.

Determination of Sulphur and Phosphorus: Absence of Titanium.

7. 0.9920 grm., treated in the way described in a previous paper (*Mineralogical Magazine*, 1894, vol. x., p. 298), yielded $BaSO_4$ 0.1481, and $Mg_2P_2O_7$ 0.0024. During these operations it was ascertained that titanium was absent.

Determination of the Alkalies.

8. 0.4815 grm., analysed by the Lawrence-Smith method, gave:—Sodium and potassium chlorides, 0.0135; tested with a small spectroscopic, only the sodium line was visible; K_2PtCl_6 (free from filter), 0.0040; adherent to filter and ignited, 0.0036.

A blank experiment simultaneously made with the same reagents gave:—Sodium and potassium chlorides, 0.0021; K_2PtCl_6 free from filter, 0.0056; adherent to filter and ignited, 0.0012.

Treatment with Mercuric Solution.

9. 4.9856 grms. were treated with mercuric solution in an atmosphere of hydrogen, as already described; the extraction proceeded for twenty-four hours and was performed three times. The first extract was appreciable; the second and third showed only slight tinges of colour.

The combined extracts yielded:—

CuS (ignited in air), 0.0003.

After oxidation of the iron and decomposition of the ammonium chloride, the residue was green, showing its comparative richness in nickel; the solution gave—

$Fe_2O_3 \cdot SiO_2$ 0.0025, yielding SiO_2 0.0004.

NiO 0.0007.

CaO 0.0040, probably almost entirely due to the action on the glass and porcelain during the precipitation of the iron and the removal of the nickel.

$Mg_2P_2O_7$ 0.0037.

Treatment with Hydrochloric Acid and Sodid Solution: First Portion.

10. 2.5065 grms. of that part of the unattracted material which had not been subjected to the action of the mercuric solution were extracted three times with dilute hydrochloric acid, according to the method described in a previous paper (*Mineralogical Magazine*, 1894, x., p. 302). In this case the extracts were decanted from the undecomposed material (admixed with free silica), and the decanted liquid and the undecomposed material separately evaporated to complete dryness; the continued action of the acid on the main material during the evaporation was thus prevented, though a certain amount of action on the finely-divided silicate suspended in the liquid cannot be avoided. The free silica was next extracted with strong solution of sodium carbonate (to which a piece of caustic soda had been added); in the last stages of the washing of the undecomposed material a little of the finely-divided silicate passes through the pores of the filter; the amount of this was afterwards determined. The sodic extract was examined, not only for silica, but for bases.

The following numbers were obtained:—

a. Undecomposed material.—Part washed from filter, 0.0186; part adherent to filter and ignited, 0.1328.

b. The acid solution yielded:—

$Fe_2O_3 \cdot Al_2O_3 \cdot SiO_2$ 0.4639; of this 0.4150, after the iron had been expelled by the Deville-Cooke method, gave $Al_2O_3 \cdot SiO_2$ 0.0055, and from this 0.0019 of SiO_2 was obtained.

MnS 0.0068.

NiO 0.0001.

The rest of the acid solution, containing the calcium and magnesium, was lost.

c. The sodic solution yielded:—

SiO_2 , with trace of undecomposed material, 0.4909. After treatment with HF and H_2SO_4 and subsequent ignition, 0.0039. The residue thus obtained was partly reddish and partly white; the

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

former was oxide of iron, the latter was found to contain magnesium; the residue was thus due to the trace of undecomposed material which had passed through the pores of the filter.

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0048, yielding SiO_2 0.0031, and the Fe_2O_3 , as judged from the colour, being small.

CaO 0.0020, partly due to action on the vessels.

*Treatment with Hydrochloric Acid and Sodid Solution :
Second Portion.*

11. 2.7333 grms. of the unattracted material, which had been subjected to the action of the mercuric solution (§ 9) and still contained mercury and mercurous chloride, treated in the above way with hydrochloric acid, gave the following:—

a. Undecomposed material.—Part washed from filter, 1.0981; part adherent to filter and ignited, 0.0516.

b. The acid solution yielded:—

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.5013; of this 0.4169 gave $\text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0044, which yielded SiO_2 0.0028.

MnS 0.0074.

NiS (after ignition in air) 0.0012.

(CaO , due to action on the vessels, 0.0022).

CaO 0.0105 (in all the analyses the calcium was twice precipitated).

SiO_2 0.0061 was obtained after the decomposition of the ammonium chloride by nitric acid, and is a measure of the amount of action on the vessels.

$\text{Mg}_2\text{P}_2\text{O}_7$ 1.3834.

c. The sodic solution yielded:—

SiO_2 , with trace of undecomposed material 0.5301.

After treatment with HF and H_2SO_4 and subsequent ignition, 0.0017.

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0065; of this 0.0046 gave $\text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0032, which itself yielded SiO_2 0.0007.

CaO 0.0013 (probably due, in part at least, to the action on the glass and porcelain).

d. Another portion, weighing 2.0583 grms., lost 0.0512 of volatile material when heated, in a current of hydrogen, in a platinum boat contained in a platinum tube supported in an oven at 208°C .; at this low temperature the troilite remains unaffected.

*Treatment with Hydrochloric Acid and Sodid Solution :
Third Portion.*

12. 2.0317 grms. of the unattracted material, which had been subjected to the action of the mercuric solution (§ 9), but from which the volatile material had been removed by heating at a low temperature in a current of hydrogen, gave the following numbers:—

a. Undecomposed material.—Part washed from filter, 0.8107; part adherent to filter and ignited, 0.0241.

b. The acid solution yielded:—

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.3775; of this 0.3352 gave $\text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0018, and the latter when analysed yielded Al_2O_3 0.0001, SiO_2 0.0016.

CuS (ignited in air) 0.0003.

MnS 0.0056.

$\text{Ni}(\text{Co})$ 0.0010.

CaO 0.0107.

SiO_2 0.0067 was obtained after the decomposition of the ammonium chloride by nitric acid, and is a measure of the amount of action on the vessels.

$\text{Mg}_2\text{P}_2\text{O}_7$ 1.0958 (and this includes the calcium and aluminium due to the action of the nitric acid on the porcelain dish).

c. The sodic solution yielded:—

SiO_2 , with trace of undecomposed material, 0.4208.

After treatment with HF and H_2SO_4 and subsequent ignition, 0.0026.

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0069; of this 0.0047 gave $\text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0022, and the latter when analysed gave Al_2O_3 0.0024, SiO_2 0.0001.

(CaO , due to action on porcelain dish, 0.0012).

(To be continued).

CORRESPONDENCE.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

SIR,—In my letter which appeared in the *CHEMICAL NEWS* of June 21st (vol. lxxxiii., p. 299) I placed on record the results of a few experiments which proved that, by boiling a solution of an ammonium salt with a slight excess of $\text{N/5 Na}_2\text{CO}_3$, a quantitative decomposition takes place, and the ammonia can thus be indirectly estimated.

It is plain to every "chemist" that, if the sample in which the ammonia is to be estimated is acid, it must first be exactly neutralised with Na_2CO_3 , and then a known quantity of $\text{N/5 Na}_2\text{CO}_3$ added. In the same way, if alkaline, it must be neutralised with acid before the estimation is proceeded with.

No doubt there are cases where this method would be useless; e.g., in highly coloured solutions it would be absurd to use an indicator.

Difficulties of this nature would be foreseen by a trained chemist, and he would alter his process accordingly.

A correspondent, Mr. McIntosh, in your issue of July 5th (*CHEM. NEWS*, vol. lxxxiv., p. 10), mentions that by this simple process he would return a sample of supposed ammonium sulphate wholly adulterated with acid sulphate of soda as containing 15 per cent of NH_4 . I think this quite possible; in fact, from the letter of July 5th more than probable. Working on the same lines it would be possible to find a certain percentage of NH_4 in a sample of pure dilute sulphuric acid.

I should be pleased to hear privately from any of your readers who have applied this method to the estimation of ammonia in commercial ammonium sulphate, manures, &c.—I am, &c.,

M. BENNETT BLACKLER.

Finsbury Technical College,
July 13, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 25, June 24, 1901.

Chemical Equilibrium. Reactions of Two Bases placed simultaneously in presence of Phosphoric Acid.—M. Berthelot.—The author investigates the reactions of two bases placed simultaneously in presence of phosphoric acid. These reactions can be divided into three fundamental cases, according to the sum of the valencies of the bases which tend to unite with one molecule of acid. This sum may be equal to one valency, R , as PO_4RH_2 ; to two valencies, R_2 , as $\text{PO}_4\text{R}_2\text{H}$; or to three valencies, R_3 , as PO_4R_3 .

Acetylo-metallic Radicles.—M. Berthelot.—A new compound can be obtained by the action of acetylene on cuprous chloride in hydrochloric solution, which corresponds to the formula $\text{C}_2\text{H}_2\text{Cu}_2\text{Cl}_2$; this, however, may be written $(\text{C}_2\text{H}_2\text{Cu})\text{Cl}.\text{CuCl}$, and is a double chloride of cupros-acetyl, corresponding to the double argentacetyl iodide and the double cupros-acetyl iodide—substances which have already been prepared.

Synthesis of a Coloured Derivative of Diphenylene-phenylmethane.—A. Haller and A. Guyot.—The authors' present researches are an attempt to solve the following problem:—Being given a coloured derivative of triphenylmethane (as, for example, crystalline violet), what modifications occur in the properties when this substance is transformed into the ortho-product of the two phenylic radicles in a coloured derivative of phenyl-fluorene?

Action of an Oxide or a Metallic Hydrate on the Solutions of Salts of other Metals; Mixed Basic Salts.—Paul Sabatier.—In a paper recently published in the *Comptes Rendus*, M. Recoura announced that he obtained directly, by contact of cupric hydrate with certain metallic salts, mixed basic salts; and he described a certain number of these compounds. The author draws attention to the fact that some time ago he undertook researches on the action of oxides or metallic hydrates produced in saline solution, and he prepared a whole series of mixed basic salts analogous to those isolated by M. Recoura.

Preparation of Phosphorous Oxide.—A. Besson.—The author prepares phosphorous oxide by dissolving hydrobromic acid gas in pure cold phosphoryl chloride; through this a stream of PH_3 gas passes. The formation of phosphonium bromide is accompanied by the deposition of a small quantity of a yellowish solid. By gently raising the temperature above 50° , and keeping the whole on a water-bath for some hours, a voluminous orange precipitate forms, which can be separated out by filtration. This, after purification, was analysed and found to possess the formula P_2O .

Action of Solar Radiation on Chloride of Silver in presence of Hydrogen.—M. Jouniaux.—When powdered silver chloride is exposed to sunlight in an atmosphere of pure hydrogen, it soon loses its white colour, gradually becoming black after passing through a series of intermediate tints. Under these conditions metallic silver is formed, at least on the surface of the particles of chloride, and it is found that hydrochloric acid gas is produced. The author finds the relative proportions of these substances after varying periods of time.

Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts.—A. Mailhe.—In a preceding paper, the author examined the action of mercuric oxide on salts of zinc, nickel, cobalt, and copper. He now continues his researches on this subject, and considers the action of mercuric oxide on salts of manganese, cadmium, lead, ferrous salts, and ferric salts.

Action of Bases and Acids on Amine Salts.—Albert Colson.—The author has already established the fact that piperidine gives, in contact with ammoniacal salts, a reaction limited by the tension of the ammonia gas. He now publishes some actual measurements of tensions, and shows that the reversibility of the reaction presents peculiarities analogous to those which have been stated with regard to the dissociation of silver carbonate.

Racemic Erythrite.—L. Maquenne and G. Bertrand.—The authors' researches confirm the accuracy of the results announced by M. Griner in 1893, and also discover the specific properties of inactive erythrite by compensation. The fusion-points of the four stereoisomers of erythrite, together with those of their characteristic derivatives, are shown in the following table:—

	Free tetrates.	Tetra-acetine.	Acetals.	
			Valeric.	Benzoic.
Inactive erythrite	+120°	+85°	Liquid	+202°
Racemic erythrite	+72°	+50–51°	+72–73°	+220°
Active erythrite	+88°	Liquid	+105–106°	+231°

The family of the tetrates is thus found in the same way as that of the pentites, defined in all the possible theoretical terms.

Action of Acid Chlorides on Aldehydes in presence of Zinc Chloride.—Marcel Descudé.—The author investigates the reaction of acetyl chloride on trioxymethylene, and of benzoyl chloride on trioxymethylene.

Nitration of Acetylacetic Ethers and of their Acidyle Derivatives.—L. Bouveault and A. Bongert.—In a preceding research, the authors prepared the two

methyl butyrylacetylacetates, and decomposed them under the influence of water and the alkalis. They now subject these two substances to the action of fuming nitric acid, and examine the products in both cases.

Acidimetric Value of Parasulphanilic Acid.—G. Massol.—Parasulphanilic acid is interesting on account of its proximity to the aromatic amine function of the mineral acid group. The acid used in the author's experiments was white and well crystalline; it volatilised without melting. The acidimetric value, using phenolphthalein, gives 100.5 per cent calculated on the formula $\text{C}_6\text{H}_4\text{NH}_2\text{SO}_3\text{H}$. The product is therefore anhydrous.

TO CORRESPONDENTS.

A. Bairstow.—The experiment seems to be a very simple one; why not try it?

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 30th; Lectures begin October 8th, 1901.

Hostels for Men and for Women Students.

Prospectuses on application to the SECRETARY.

HERIOT-WATT COLLEGE, EDINBURGH.

DAY TECHNICAL COLLEGE.

Three Years' Courses of Instruction in MECHANICAL ENGINEERING, ELECTRICAL ENGINEERING, TECHNICAL CHEMISTRY.

The Classes for the Diploma in Mechanical and Electrical Engineering are recognised by the University of Edinburgh, and Students wishing to obtain a B.Sc. in Engineering, as well as the Diploma, can qualify for the Degree by taking five additional courses in the University and passing the University examinations.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with special courses in Gas and Paper manufacture, Brewing, &c., by experts, in the third year. Special attention will be paid to Electro-chemistry.

Session, from October to June. Matriculation fee, 5s.; Composition fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN that

GEORGE WILLIAM JOHNSON, of 47, Lincoln's Inn Fields, in the County of London, has applied for leave to amend the Specification of Letters Patent No. 24748 of 1899, granted to him for "Improvements in the Manufacture or Production of Sulphuric Anhydride and means to be employed therein."

Particulars of the proposed amendment were set forth in the "Illustrated Official Journal" (Patents) issued on the 10th July, 1901.

Any person or persons may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

C. N. DALTON,
Comptroller-General.

JOHNSONS & WILCOX,
Agents,
47, Lincoln's Inn Fields,
London, W.C.

FOR SALE.—Two Becker's Balances, Water-bath, Agate Mortar, and sundry pieces Apparatus; good order; cheap.—Address, John Lochhead, 16, Bothwell Street, Glasgow.

THE NEW EXPLOSIVES CO., LTD., 75, Queen Victoria Street, London, E.C., are prepared to receive DESIGNS and ESTIMATES for the erection at their Stowmarket Factory of a CONCENTRATION OR RECOVERY PLANT, capable of treating 50 tons of Waste Acid per week from the manufacture of Gun-cotton.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2174

ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA.*

By G. D. LIVEING, M.A., Sc.D., F.R.S.,
Professor of Chemistry in the University of Cambridge,
and

JAMES DEWAR, M.A., LL.D., F.R.S.,
Fullerian Professor of Chemistry, Royal Institution, London.

OUR last communication to the Society (*Roy. Soc. Proc.*, vol. lxvii., p. 467), related to the most volatile of the atmospheric gases; that which we now beg leave to offer relates to the least volatile of those gases. The former were obtained from their solution in liquid air by

fractional distillation at low pressure, and separation of the condensable part of the distillate by cooling it in liquid hydrogen. The latter were, in the first instance, obtained from the residue of liquid air, after the distillation of the first fraction, by allowing it to evaporate gradually at a temperature rising only very slowly. The diagram, Fig. 1, will make the process intelligible. A represents a vacuum-jacketed vessel, partly filled with liquid air, in which a second vessel, B, was immersed. From the bottom of B a tube, *a*, passed up through the rubber cork which closed A, and from the top of B a second tube, *b*, passed through the cork and on to the rest of the apparatus. Each of these tubes had a stopcock, *m* and *n*, and the end of tube *a* was open to the air. A wider tube also passed through the cork of A, and led to an air-pump, whereby the pressure above the liquid air in A was reduced, and the temperature of the liquid reduced by the consequent evaporation. To keep the inner vessel, B, covered with liquid, a fourth tube, *r*, passed through the cork, and its lower end, furnished with a valve, *p*, which could be opened and closed by the handle, *q*, dipped into liquid air contained in the vessel C. As the

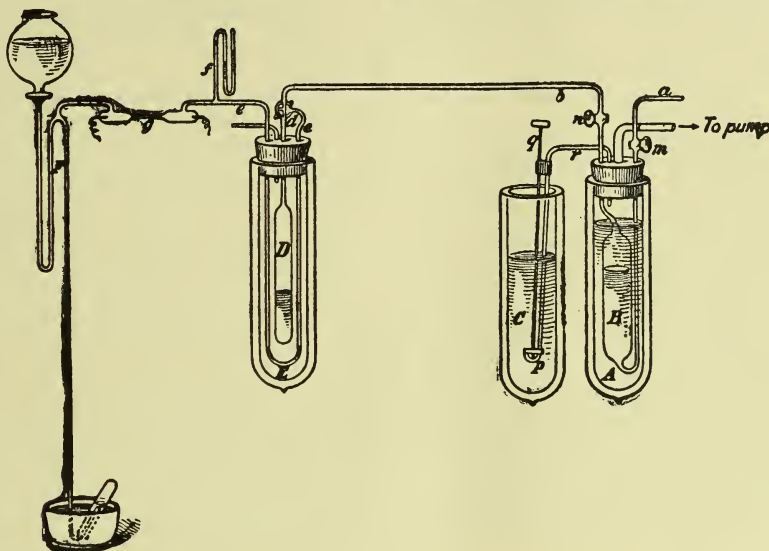


FIG. 1.

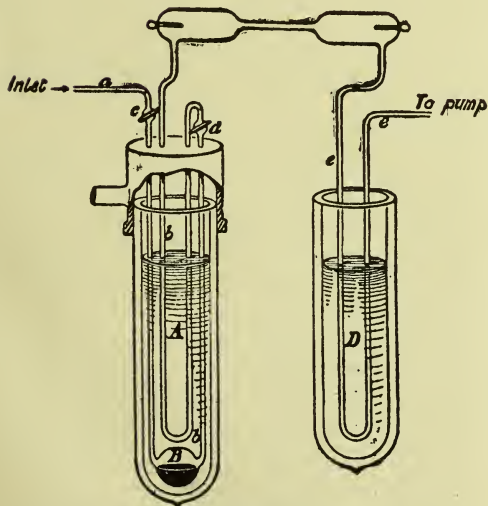


FIG. 2.

pressure above the liquid in A was less than that of the atmosphere on opening the valve, *p*, some of the liquid air was forced through *r* into A by the pressure of the atmosphere, and in this way the level of liquid in A maintained at the required height.

Since B was maintained at the temperature of liquid air boiling at reduced pressure, the air it contained condensed on its sides, and when the stopcock *n* was closed and *m* opened, more air passed in through the open end of *a*, and was in turn condensed. In this way B could be filled completely with liquid air, the whole of the most volatile gases being retained in solution in the liquid.

The tube, *b*, passing from the top of B, was connected with a three-way stopcock, *d*, by which it could be put in communication with the closed vessel, D, or with the tube *e*, by which also D and *e* could be connected. The tube *e* passed down nearly to the bottom of the vacuum-jacketed vessel E, and out again through the cork; and on to a gauge *f*, and through a sparking tube *g* to a mercury pump F. The stopcock *n* being still closed, the whole of the apparatus between *n* and the pump, including the vessel D, was exhausted, and liquid hydrogen introduced into E. The three-way cock, *d*, was then turned so as to connect *c* with D, and close *e*, and then *n* opened. B was thereby put in communication with D, which was at a still lower temperature than B, and the gas dissolved in

* A Paper read before the Royal Society, June 20, 1901.

the liquid in B, along with some of the most volatile part of that liquid, distilled over, and the latter condensed in a solid form in D. When a small fraction of the liquid in B had thus distilled, the stopcock *d* was turned so as to close the communication between D and C, and open that between D and E. Gas from D passed into the vacuum tubes, but in so doing it had to pass through the portion of E which was immersed in liquid hydrogen, so that condensable matter carried forward by the stream of gas was frozen out.

For separating the least volatile part of the gases the vessel E, with its contents, was dispensed with, and the tube C made to communicate directly with that connected with the gauge, sparking tube, and pump; and generally several sparking tubes were interposed between the gauge and pump, so that they could be sealed off successively. The bulk of the liquid in B consisted of nitrogen and oxygen. These were allowed gradually to evaporate, the temperature of B being still kept low so as to check the evaporation of the gases less volatile than oxygen. When a great part of the nitrogen and oxygen had thus been removed, the stopcock *n* was closed, and the tubes partially exhausted by the pump, electric sparks passed through *g*, and the gases examined spectroscopically. More gas was then evaporated from B, and the spectroscopic examination repeated from time to time.

The general sequence of spectra, omitting those of nitrogen, hydrogen, and compounds of carbon, which were never entirely removed by the process of distillation alone, was as follows:—The spectrum of argon was first noticed, and then as the distillation proceeded the brightest rays, green and yellow, of krypton appeared, and then the intensity of the argon spectrum waned, and it gave way to that of krypton until, as predicted by Runge, when a Leyden jar was in the circuit, the capillary part of the sparking tube had a magnificent blue colour, while the wide ends were bright pale yellow. Without a jar the tube was nearly white in the capillary part, and yellow about the poles. As the distillation proceeded, the temperature of the vessel containing the residue of liquid air being allowed to rise slowly, the brightest of the xenon rays began to appear, namely, the green rays about λ 5420, 5292, and 4922, and then the krypton rays soon died out, and were superseded by the xenon rays. At this stage the capillary part of the sparking tube is, with a jar in circuit, a brilliant green; and is still green, though less brilliant, without the jar. The xenon formed the final fraction distilled.

Subsequently an improved form of apparatus was used for the fractionation. It is represented in Fig. 2. A gas-holder containing the gases to be separated, that is to say, the least volatile part of atmospheric air, was connected with the apparatus by the tube *a*, furnished with a stopcock *c*. This tube passed on to the bulb B, which in turn communicated through the tube *b* and stopcock *d* with a sparking tube, and so on through the tube *e*, with a mercurial pump. (The Sprengel in figure is simply diagrammatic). Stopcock *d* being closed and *c* opened, gas from the holder was allowed to pass into B, maintained at low temperature, and there condensed in the solid form. Stopcock *c* was then closed and *d* opened, and gas from B allowed to pass into the exhausted tubes between B and the pump. The tube *e* was partly immersed in liquid air in order to condense vapour of mercury, which would otherwise pass from the pump into the sparking tube. The gas passing into the sparking tube would, of course, have a pressure corresponding to the temperature of B, and this was further ensured by making the connecting tube pass through the liquid in which B was immersed. The success of the operation of separating all the gases which occur in air, and which boil at different temperatures, depends on keeping the temperature of B as low as possible, as will be seen from the following consideration.

(To be continued).

THE PHARMACOLOGY OF PYRACONITINE AND METHYLBENZAONINE CONSIDERED IN RELATION TO THEIR CHEMICAL CONSTITUTION.*

By J. THEODORE CASH, M.D., F.R.S.,
Regius Professor of Materia Medica in the University of Aberdeen,
and
WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Scientific Department of the Imperial Institute.

In a previous paper (*Phil. Trans.*, 1898, pp. 190, 239), we have shown that an entire change in the physiological action ensues on the withdrawal of the acetyl group from aconitine as is seen in the action of benzaconine, the first hydrolytic product of aconitine, from which it differs in containing an atom of hydrogen in the place of one acetyl group. This alkaloid is devoid of the characteristic physiological action and extraordinary toxicity of aconitine, whilst in respect of its action on the heart it is in the main antagonistic to that of the parent alkaloid. In order to study further the remarkable dependence of the physiological action on the presence of the acetyl group we have examined the action of two derivatives of aconitine which we have obtained in this research, viz., pyraconitine and methylbenzaconine.

Pyraconitine was first prepared by one of us (Dunstan and Carr, *Trans. Chem. Soc.*, 1894, vol. lxx., p. 176), by heating aconitine at its melting-point, when the acetyl group is expelled as one molecule of acetic acid, and the alkaloid pyraconitine remains. This compound therefore differs in composition from aconitine by the loss of one molecule of acetic acid, and from benzaconine by one molecule of water.

Methylbenzaconine was obtained from aconitine by heating it with methyl alcohol in a closed tube (*Proc. Chem. Soc.*, 1896, p. 159). A remarkable reaction takes place, in which the acetyl group is ejected as acetic acid, a methyl group taking its place. This alkaloid therefore differs from aconitine in containing a methyl group in the place of the acetyl group, and from benzaconine in containing a methyl group in the place of one atom of hydrogen. The examination of its physiological action would therefore be the means of studying the result of replacing in aconitine the negative radical acetyl by the positive methyl group, and also of studying the effect of the introduction of methyl in modifying the physiological action of benzaconine.

The acetyl group of aconitine evidently occupies an exceptional position in the molecule of aconitine. So far as we are aware, it is the only acetyl compound at present known which exchanges this group for methyl when it is heated with methyl alcohol. We have examined the behaviour of numbers of different types of acetyl derivatives from this point of view, and can find none analogous to aconitine.

For the study of their physiological action these alkaloids have been specially purified and employed as hydrobromides in aqueous solution.

Contrasting the physiological action of pyraconitine with that of aconitine, as described in the present paper, we find, as might be anticipated from our previous results, that through the removal of the acetyl group the great toxicity of aconitine is nearly entirely abolished, and the characteristic features of aconitine poisoning are no longer produced by pyraconitine.

Contrasting the physiological actions of benzaconine and pyraconitine which differ from each other empirically by one molecule of water, pyraconitine, the anhydride, is the more active compound. Both these alkaloids, divested of the acetyl group of aconitine, are relatively weak, and feebly toxic when compared with the parent alkaloid.

Although benzaconine and pyraconine exhibit a strong similarity in the physiological effects they produce, there are differences between them which are probably more

* Abstract of a Paper read before the Royal Society, June 20, 1901.

considerable than they would be if pyraconitine were merely the anhydride of benzaconine.

The substitution in aconitine of methyl for acetyl which occurs in the formation of methyl benzaconine has led to a very considerable reduction in toxicity, and has introduced a curare-like effect similar to that first observed by Crum Brown and Fraser (*Trans. Roy. Soc. Ed.*, 1869, vol. xxv., 192), to result from the introduction of methyl into the molecule of an alkaloid. Methyl benzaconine is, however, more toxic and generally more powerful than benzaconine, owing to the presence of the methyl group.

Action of Pyraconitine.

The main effects of pyraconitine may be thus summarised. Its local application is devoid of the effects characteristic of the aconitines. Its chief action upon the heart is to cause slowing, partly from vagus irritation, partly from depression in function of intrinsic rhythmical and motor mechanisms.

There is less tendency to want of sequence in the cardiac chamber walls than is observed after the aconitines and benzaconine.

The vagus apparatus remains active in degree after doses somewhat in excess of the lethal, the slowed heart of pyraconitine being accelerated both by vagotomy and by atropine.

Activity of respiration is reduced (by central depression) to a degree incompatible with life, as is the case after aconitine and benzaconine. The peripheral motor nerves and muscular tissues are not at this time markedly affected. Artificial respiration prolongs life, but the slowed heart and greatly reduced blood pressure tend to a fatal issue.

The spinal cord is impaired in its reflex function, apparently secondarily to reduced circulation in its structure. A tendency to tonic spasm in frogs is late in appearing, and of moderate degree. It has not been seen after destruction of brain and medulla. It is further associated with a curious condition of exaggerated motility.

Neither muscular nor intramuscular nervous tissue are strongly influenced by pyraconitine in lethal or somewhat hyperlethal doses. The lethal dose per kilo. frog's weight is practically about twelve times that which is lethal per kilo. rabbit's weight.

Contrasted Effects of Pyraconitine and Benzaconine.

Of these two alkaloids, pyraconitine is approximately six to seven times more toxic towards mammals (rabbits and guinea-pigs) than benzaconine, and five to six times more so towards frogs. They are alike in their action upon mammals, in so far as they are non-irritant, that they slow the respiration without preliminary acceleration, that they slow the heart and reduce the blood pressure to a very low level, that they cause paresis, and in guinea-pigs clonic movements, and that respiratory failure is the immediate cause of death. They differ in so far that pyraconitine acts more rapidly, but for a shorter period, whilst fatal termination of poisoning is preceded by convulsions, which are very rare after benzaconine. Benzaconine alters the sequence of the ventricles upon the auricles much more usually and to a greater extent than pyraconitine, though if a sequence is developed it has the same general character (the auricular second beat being blocked from the ventricle).

Whilst pyraconitine stimulates the cardiac vagus both centrally and within the heart and finally occasions only a limited reduction in its activity, benzaconine produces but little stimulation, and ultimately suspends the vagus inhibitory action. Under these conditions atropine is, of course, inoperative. Both accelerate the heart in small, but slow it in large, dose, and both may disorder the sequence, but vagus inhibition is much more interfered with by benzaconine. Frogs poisoned by benzaconine lose the power of voluntary movement, then reflex disappears, and finally the circulation is arrested; but after pyraconitine, reflex

outlasts the heart's action. Late spasm occurs after the latter, not after the former. Whilst in lethal doses pyraconitine has no effect beyond somewhat favouring fatigue and reducing excitability of motor nerves, benzaconine greatly impairs their function, and in thorough poisoning may suspend it entirely.

Action of Methylbenzaconine.

The action of methylbenzaconine may be summed up as follows:—It is very feeble in its toxicity when contrasted with aconitine, but is somewhat stronger than benzaconine.

Small and medium doses, whilst slowing the heart, do not cause any failure in sequence, but larger doses have this effect. They act upon the rhythm of the organ, involving the movement of the auricle and ventricle, whilst ultimately the sequence of the latter upon the former is impaired, so that it follows only a certain proportion of the auricular "leads." This block is not removed by atropine. Whilst the passage of the ventricle into the diastole is at first retarded, the contractile power of the myocardium is ultimately reduced by methylbenzaconine.

The cardiac vagus is depressed in action and its inhibitory function is ultimately suspended by large doses, neither section of the vagus nor atropine administration relieving the slow and faulty action of the organ.

There is evidence of slight primary stimulation of reflex cord centres when ligature of vessels prevents the masking of this condition by the peripheral action of the poison. The subsequent impairment in cord reflexes is later in occurring and of much shorter duration than the action of methylbenzaconine upon intramuscular motor nerves.

In mammals the paralytic symptoms are predominant, the fall of temperature is in part attributable to this cause as well as to changes in the circulation. The clonic movement and salivation (observed in a certain stage of the action of methylbenzaconine, especially upon guinea-pigs) are suggestive of the action of a near ally of aconitine. In frogs, however, there is no semblance to an aconitine effect, unless its very feeble action towards sensory nerves or its much more powerful action upon motor nerves, be thus viewed. Motor nerves are greatly affected by doses which are distinctly below the lethal for cold-blooded animals, the action being curare-like in character. Muscular tissue is after the action of large doses more susceptible of fatiguing influences. Fibrillation in muscles to which the poison has access is more common than after aconitine or any other derivative examined.

These observations support in the main the contention of Crum Brown with Fraser that the introduction of methyl into the molecule of certain spasm-producing alkaloids, marks the effect of these by occasioning a curare-like action at the periphery.

Contrasted Effects of Methylbenzaconine and Aconitine.

The toxicity of aconitine is, roughly, eighty to one hundred times that of methylbenzaconine towards rabbits and guinea-pigs, and much the same proportion holds for summer and winter frogs respectively. Whilst slight tendency to salivation and retching movements are produced by methylbenzaconine, and are in so far suggestive of a slight aconitine action, the absence of initial acceleration of respiration, of local irritation, and dyspnoeal convulsions, and the predominance of paralytic symptoms, are points of difference. The action upon the heart is entirely distinct, for the pulse is slowed by methylbenzaconine, the auricles eventually beating more rapidly than the ventricles, the action of the poison proceeds uniformly and without the intermissions which characterises aconitine, whilst the early phenomena of vagus stimulation have little in common. The general symptoms of poisoning in frogs have scarcely a point of similarity, quiescence, rapid failure of reflex, and voluntary movement, without impairment of the cardiac action, are distinctive of methylbenzaconine, whilst excitement with great motility and persistence of voluntary movement

follow aconitine. Fibrillation is much more pronounced after the former, though it is only a transitory phenomenon. The action on the heart differs widely in frogs as it does in mammals, whilst the curare-like action of the derivative on motor nerves is not produced by aconitine in doses which just suffice to arrest the heart.

It is true that large but sublethal doses of aconitine are followed by a condition of almost complete paralysis, which lasts for several days, but during this time there is slight voluntary and reflex movement, the nerve-endings are not put out of action, and the circulation is usually of the feeblest character, all conditions which are not found in the period of quiescence following methylbenzaconine.

Contrasted Effects of Methylbenzaconine and Benzaconine.

Methylbenzaconine is from three to four times more toxic towards rabbits and guinea-pigs than benzaconine, and from twice to thrice as toxic towards frogs (*R. temp.* and *R. esc.*). In mammals, slight salivation, retching movements, and muscular tremor are characteristic effects of the former, but dyspnoea, ataxia, and paresis are also seen after benzaconine. Of the two, methylbenzaconine is distinctly less depressant towards the heart. Slowing of the pulse and want of sequence of ventricular upon auricular action occurs after both, but is a much earlier symptom after benzaconine, which causes more disorder in the motor mechanism. On the other hand, the intracardiac vagus is put out of function more readily by methylbenzaconine. Death after either poison is rarely preceded by spasm. Neither of the two compounds cause any local irritation in frogs, but methylbenzaconine produces active fibrillation in the muscles, to which it gains access and develops a complete curare-like action much more prominently than does benzaconine, the heart continuing to beat strongly. Benzaconine, in dose sufficient to cause such an effect at the periphery, acts disastrously upon the circulation. In partial poisoning by methylbenzaconine the characteristic rapid failure of the intramuscular motor nerves on stimulation is well marked, but the subsequent recovery on resting, so characteristic of benzaconine, has not been observed.

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 32).

Covering the Plates.—This must be performed as soon as possible after laying the plates on the level mirror glass and filtering the emulsion. One pours over little plates immediately out of the supply-flask, which is held with its opening very near the receiving surface to avoid the formation of bubbles; with larger plates the quantity of emulsion for each plate is measured off. In the first case the emulsion is poured on till the plate is covered with it—50 to 60 c.c. are necessary for plates 13×18 c.m. For the plates for my own use—which measure only 9×13 c.m.—I need 25 c.c. One must always endeavour to cover the nearer corners, those on the side of the operator, before the further ones, for sometimes the emulsion flows slowly, and does not reach all the corners. Then, instead of adding an excess of emulsion, it is better to assist the covering of the corners by carefully and gradually raising the opposite side of the plate. And this is more readily carried out on the near side than on the other. Whilst doing this, one must avoid disturbing the edge, and should rather press against the underside of the mirror.

Deposition of Silver Bromide for Formation of the Sensitive Film.—The covered plate must be protected from dust during the hours of deposition of the silver bromide; it is also advisable to check as far as possible all evaporation, so as to preserve the original concentra-

tion of the emulsion. I attain both objects by covering the mirror glass, on which the plates stand, with a large pasteboard box covered on the inside with shellac varnish, and excluding all light. The temperature of the room, during formation of the film, should not be below 18° C. In three to four hours there is a sufficient deposition of silver bromide. There is a supernatant layer of emulsion, poor in silver, and of milky aspect, which can be poured off without detriment to the film. This is the only part of the whole process which demands special attention in order to secure a successfully prepared plate.

To Pour off the Emulsion.—This is conducted in the following manner, always beginning with the first plate on the left, the glass mirror being in front of the operator:—The plate is now pushed out over the nearest (left) edge of the supporting surface, till about $\frac{1}{10}$ of its length projects. Beneath this is placed a deep evaporating dish, which is 1 to 2 c.m. wider than the plate. If the plate is now raised from beneath with the first finger of the left hand, high enough for it to turn about the margin of the mirror plate, its free end sinks into the dish, whereby the emulsion flows off over both corners, and one can take hold of the plate by the edges of the raised corners, remove it, and stand it up to dry upon a board covered with blotting-paper, and bearing a row of vertical wooden rods, against which the plate leans with the film side downwards. In pouring off the emulsion and placing the plates on the drying board, the plates should be held to prevent the formation of streaks, so that the emulsion flowing along the edge cannot trickle across the silver bromide coating. The streaks thus confine themselves to the immediate neighbourhood of the margin, and may be cut away, but which do not affect the larger plates.

To Dry the Film.—The drying of the plate may be carried out in a room free from dust, or in a drying cupboard. The latter is preferable as the film is very sensitive to air currents, which produce zones of drying, and these show themselves in the negative as varying intensity in the film and noticeable lines. The tendency to formation of zones is greater in this film, which dries very quickly, than in the ordinary gelatin dry plate. A quarter of an hour is sufficient for drying under some circumstances. In my dry cupboard, which in this case I do not ventilate, these plates require from half to three quarters of an hour. If the plate is required for exposure as soon as possible it may without hesitation be wiped with a strip of blotting-paper.

To keep the Plates.—I lay my plates together in pairs, film against film, with a narrow strip of blotting-paper between the edges, and wrap them up in black paper. It is best not to put more than one pair together in a packet, on account of possible damage to the film. The packets are stored in a plate cupboard or a light-tight box in a dry place.

Unpacked plates tend to become fogged sooner than those in packets. But plates which are to be used shortly after preparation may be kept without packing from eight to fourteen days in a light-tight place. But I must add a warning against tin-plate receptacles. This metal seems to cause fogging even without direct contact.

The Dry Plate.—Its colour is milky white, with a touch of green, in reflected light, and dark yellow in transmitted light, and the film less pure than it appears to be in the former case. Even after innumerable attempts I have not yet succeeded in preparing such homogeneous films as can be obtained with the silver bromide gelatin plate. With the most careful cleansing of the emulsion, and observing the greatest cleanliness throughout, it still shows differences in intensity, dark spots, and sometimes holes like pin-pricks. If it is compared in transmitted light with an ordinary dry plate, it gives very little impression of trustworthiness, on account of its transparency and the thinness (0.003 – 0.004 m.m.) of its film. The attempt to gauge its spectrographic value in this way would result in a very unfavourable judgment of its adaptability to exact

* *Annalen der Physik*, 1901, vol. v.

spectral uses. But experience has proved that the opposite is the case, that these film blemishes in no way spoil the purity and definition of the spectrum lines, as they only appear in the negative when the plate is too old and is already fogged.

The plate is specially sensitive towards mechanical impressions. Thus it cannot even bear dusting with a brush; the finest hair leaves traces which are obvious before developing, and more so afterwards in the negative, where they appear as fine black lines.

For the same reason it requires, on cutting, very careful handling. It is best cut through the film, when narrow strips of paper, not too thin, should be laid upon the edge of the plate under the ruler which guides the diamond. One must beware that the strips of paper may leave behind spots which develop simultaneously with the picture. Therefore the strips should be so narrow that the part of the film which is to receive the spectrum may not be injured.

The Stability of the Plate.—For the first few days after preparation the plate is not very sensitive and it lacks intensity. Therefore at this time it needs unusually strong developers, solutions of a concentration which could not be used for the dry plate for fear of fogging. In this case there is no fear of displacing the film. The coating of the plate exhibits great resistance capacity towards certain chemicals. Fuming nitric acid, concentrated sulphuric, hydrochloric, and potash solution 1:3, &c., do not attack it. Fuming nitric acid destroys neither the latent nor the developed picture. The acid merely diminishes the intensity. This behaviour of the film is all the more remarkable in that gelatin, which is one of the constituents of the film, is easily soluble in nitric acid. We must conclude from this that the degree of solubility of the gelatin is in this case dependent on the thickness of the film.

The plate increases by keeping in sensitiveness and intensity; one to two weeks after the preparation, both give evidence of a marked increase, and there is a further increase especially exhibited in the latter. Plates one to two months old have given me the best results. In the third month there are already traces of fog. But by a large addition of potassium bromide to the developer transparent negatives can still be obtained. Plates stored in dry air have even kept faultless for nearly two years, but with these there is a noticeable decrease of sensitiveness. As the clearness of the picture in this case depends upon a further increase in the addition of potassium bromide, which lengthens the time of exposure, I cannot recommend so old a plate.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

(Continued from p. 31).

WHERE not otherwise stated, the appended results following refer to a mixture of three parts ether (sp. gr. 0.720) and one part alcohol (sp. gr. 0.810). But, as will be demonstrated later, the same results may also be obtained with numerous other proportions of the mixture.

For the determination of unchanged cellulose and oxy-cellulose cf. Part B.

A. Influence of Water upon the Process of Nitration.

The principal factors in the production of nitrocellulose are the relative proportions of nitric acid, sulphuric acid, and water; this relation determines in great degree the result of nitration. Since many of the stages of nitration of cellulose have been put to great industrial use, the necessity has arisen of knowing as nearly as possible the different mixture proportions of those three bodies in their

influence upon the progress of nitration. It is naturally impossible to examine individually all the innumerable possible combinations; but it ought to be possible to gain an accurate insight into these complex relations by means of numerous systematically arranged series of experiments.

Vieille was the first to undertake a research with this intention. He started with a sulphuric acid of sp. gr. 1.832, and mixed one part of the same with different quantities respectively of a nitric acid of sp. gr. 1.316. In this manner he obtained, from twelve different proportions, nitrocelluloses containing from 132.7 to 195.9 c.c. NO. In this method of nitration there are therefore two variable quantities, nitric acid and water, and the results obtained must therefore be considered as due to the action of these two factors. We notice the same in the research carried out later by Bruley. His results afford a survey of the influence of a great number of combinations of nitric acid, sulphuric acid, and water; but, on the other hand, the absolute action of any one of these three factors is only visible in them to a limited extent. But this knowledge should be of value for further researches, and it was the object of the first part of this work to obtain it.

Next, therefore, it was necessary to determine the influence of the water upon the process of nitration in the least ambiguous manner possible, for which purpose the following method was pursued:—The nitration mixture consisted of equal parts by weight of sulphuric acid 1.83 and nitric acid 1.5 (free from lower nitrous oxides). Equal portions of this were now treated with varying quantities of water. Therefore the ratio of nitric acid to sulphuric acid was the same in all the nitration mixtures. The remaining factors, *e.g.*, temperature, time of nitration, relation of the cellulose to the amount of nitric acid contained in the mixture, were kept as constant as possible; hence the water was the only variable, and the results are entirely traceable to the action of this one factor.

The temperature was that of the surroundings, *i.e.*, 16–18° C.; the time of nitration lasted twenty-four hours. The cellulose material used was “chemically pure dressing wadding.” This was boiled with dilute soda solution, well washed, and finally treated with alcohol and ether; then dried at 100° before nitration, and cooled down in the desiccator. The nitration was generally conducted in wide-necked, well-stoppered glass cylinders, but nitrations at raised temperatures in the apparatus described by Lunge and Weintraub.

After twenty-four hours the nitration mixture was poured off, the nitration product pressed upon porous porcelain to free it from most of the adhering acid, and then placed in small portions in much cold water, afterwards laid upon a porous plate, treated for some time with cold water, and finally washed with hot water as often as possible for two days.

The examination of the products obtained comprised the percentage of nitrogen, solubility in ether-alcohol, and behaviour towards polarised light. Besides this, we give the corresponding gain of nitrocellulose in 100 parts of pure cellulose used.

The accompanying table contains the results of this first series of experiments, and the analyses of the corresponding nitration mixture. These were conducted according to the commonly used methods. One test gave the total acid by titration, the other the sulphuric acid by evaporating off the nitric acid on the water-bath; the percentage of nitric acid was obtained by difference.

It may be here once for all mentioned that the numbers quoted in this work have been obtained in each case from at least two experiments agreeing well with each other.

The nitration products obtained do not, as a rule, represent individual compounds, but mixtures of different nitrocelluloses. The property of partial solubility of the products in ether-alcohol points with certainty to this fact; this was therefore used to effect a partial separation of the nitration products. Certainly the soluble portion, as also the insoluble, may again consist of a mixture of different

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

Expt.	C.c. NO per 1 grm.	Per cent N.	Solubility in ether- alcohol (3:1).	Gain.	Nitration mixture.		
					H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	217.73	13.65	1.50	177.5	45.31	49.07	5.62
2.	210.68	13.21	5.40	176.2	42.61	46.01	11.38
3.	203.49	12.76	22.00	—	41.03	44.45	14.52
4.	200.58	12.58	60.00	167.0	40.66	43.85	15.49
5.	196.35	12.31	99.14	159.0	40.14	43.25	16.61
6.	192.15	12.05	99.84	153.0	39.45	42.73	17.82
7.	184.78	11.59	100.02	156.5	38.95	42.15	18.90
8.	174.29	10.93	99.82	144.2	38.43	41.31	20.26
9.	155.73	9.76	74.22	146	37.20	40.30	22.50
10.	148.51	9.31	1.15	138.9	36.72	39.78	23.50
11.	133.94	8.40	0.61	131.2	35.87	38.83	25.30
12.	103.69	6.50	1.73	—	34.41	37.17	28.42

nitrocelluloses; but it often happened that—judging by the proportion of nitrogen—one or both of the components were single bodies. In the case of those products which contained only a small percentage of either soluble or insoluble components, it was necessary to dispense with a separate examination of both portions on account of lack of material, and only that portion was examined which contained the predominating amount; the percentage of nitrogen contained in the other portion being determined by calculation.

If, for example, the percentage of nitrogen of the insoluble portion has been determined, and we put—

- a = c.c. NO per 1 grm. mixture;
- b = c.c. NO per 1 grm. insoluble portion;
- c = percentage solubility in ether-alcohol;
- d = percentage N of the soluble portion;

then we have—

$$d = \frac{100(a-b) + b.c}{c}.$$

If, however, the quantity d has been already determined, we find the quantity b from—

$$b = \frac{100a - d.c}{100 - c}.$$

But one must pay attention to the fact that the solubility determination is not very exact, especially in cases where there is only a small proportion of soluble constituents, and that, therefore, this indirect nitrogen determination cannot claim the same accuracy as the direct.

Experiment 1 yielded a product with a remarkably high percentage of nitrogen. Although the nitration mixture was not very concentrated, containing 5.6 per cent water, yet we surpassed the nitrogen content of 214 c.c., designated by Vieille as the maximum. In Section C, "The Highest Degree of Nitration attainable by means of Mixtures of Nitric Acid and Sulphuric Acid," this result is explained. The percentage of nitrogen in the product extracted with ether-alcohol was but little higher, viz., 218.00, and that of the soluble portion accounted for 200.00 c.c. NO.

The result of increasing the proportion of water is at first—up to about 11 per cent—only a slight diminution in the contained nitrogen. From the graphical representation of the results, the gradually increasing influence of the contained water is clearly visible.

The insoluble portion of the product obtained in Experiment 2 shows a proportion of nitrogen near to that of hendeca-nitrocellulose, viz., 213.25 c.c.; that of the soluble part is, by calculation, 181.4 c.c.

Experiment 3 gives a product with a percentage of nitrogen agreeing with that of decanitrocellulose. But its merely partial solubility shows it to be no simple body. The soluble portion proved to be octanitrocellulose (177 c.c. NO), while the insoluble portion gave a nitrogen percentage of 211.5 c.c. (calculated 211.00). It is clearly obvious that the percentage of nitrogen alone does not suffice to identify a nitration product. Hence the properties of a nitrocellulose, whose percentage of nitrogen

corresponds to a certain stage of nitration, should not—as has often happened—be ascribed to the latter without further confirmation.

The above experiments show a somewhat large difference in the degree of nitration of the two components (insoluble and soluble portion). This might be chiefly ascribed to the dilution of the nitration mixture which sets in during the course of the reaction, and which is caused partly by the abstraction of nitric acid, and partly by the development of the water of reaction. But, as is to be inferred from this series of experiments, small percentage differences in the water content produce considerably different stages of nitration, and it is therefore easy to comprehend that during nitration no single bodies arise, but mixtures of different nitrocelluloses. The greater the mass of the nitration mixture compared with that of the cellulose, the less is the absolute change in the composition of the mixture, and hence the smaller the influence of this change on the process of nitration. Thus it appears also that the ratio of the mass of the cellulose to that of the acid mixture plays a not unimportant part.

(To be continued.)

THE CRYSTALLISATION OF COPPER SULPHATE.

By ARTHUR JOHN HOPKINS.

The Size of Crystals.

THE work described in this paper had for its object the preparation of crystals of copper sulphate, which should be from 20 to 30 m.m. in length. The first part contains a short discussion of those general conditions which determine the size of crystals, together with a development of a method for the preparation of crystals of any desired size. The following principles guided the work:—

I. In the process of crystallising copper sulphate, at constant room temperature, the solubility is a constant, and the concentration (weight of solute in unit volume), minus this constant is the total weight of crystal deposit. Or, in other words, in the process of crystallising copper sulphate at constant room temperature, the concentration determines the weight of the crystal deposit.

II. (a) In a solution, supersaturated in absolute quiet, no crystals will form.

(b) In a solution supersaturated in absolute quiet, the number of crystal points formed by the first disturbance (if the disturbance is succeeded by quiet) is the same as the number of crystals finally formed.

(c) The ratio between the number of crystals formed and the weight of crystal deposit determines the size of the crystals.

III. For a given volume of solution and given size of crystals, and weight of crystal deposit, the diameter of the crystallising dish determines the space between the crystals.

The usual laboratory practice of preparing a solution of known concentration with the expectation of getting crystals of definite size is therefore misleading, as this method gives only one definite result, *i.e.*, a certain weight of crystal deposit, as is expressed by the first principle. From principle II. it is clear that the number of crystals to be formed is determined almost instantaneously, *i.e.*, that nothing in the previous history of the solution (its concentration, the size of the dish, or the rate of cooling) directly determines the number of crystals, but that as the solution cools beyond the point of saturation, a few crystal points suddenly started, whether by direction or accidentally, will slowly grow by addition from the solution, and, if given equal opportunity, will grow equally, each crystal's final weight becoming the quotient of the total weight of crystals deposited, divided by the number of points started.

Again, from the third principle, it is evidently desirable that the dish be large enough to allow the crystals full room to grow without crowding.

The experiments of the two parts of this paper number about 60. The first experiments are passed over. They proved that neither concentration alone, nor the relation of the size of the dish to the volume of the solution, nor the rapidity of cooling determines the size of the crystals. These facts were all proved later by two experiments, as follows:—First, bring a solution of definite volume and concentration to supersaturation in absolute quiet, and then, after disturbing, note the size of crystals formed. Second, after warming the crystals and the solution obtained as described, repeat the first experiment, when crystals of an entirely different size will probably be deposited. A single such experiment shows that the slightest accident, after saturation, may determine the size of crystals.

In all of this work, dust was excluded as rigorously as possible by careful filtering of solutions and scrupulous cleaning of crystallising and other dishes. In order to prevent carbonate from forming and acting as centres of crystallisation, recently boiled water was used at first, then water known to be free from carbonic acid, but finally it was found necessary (in continued crystallisations of the same solution), to add about 5 c.c. of normal sulphuric acid to every 100 c.c. of solution. Uniformity in measuring (without danger of error due to contraction on cooling to indefinite degrees), was approximated by concentrating the filtered and perfectly clear solution in a marked beaker to a volume smaller than that desired, pouring quickly into a hot measuring cylinder, transferring the last drops by aid of a little boiling water, filling the cylinder to the desired volume with boiling water, and pouring the solution quickly into a clean crystallising dish, which was immediately covered. All of these experiments were conducted in a room held at constant temperature by a heat regulator, and a watch was kept on the indications of a maximum and minimum thermometer. A variation of 2° was unusual, and occurred only during the night.

Experiments showed that solutions of convenient concentration and volume were obtained, when 171 grms. of clean copper sulphate crystals were dissolved in water and 15 c.c. of normal sulphuric acid were added, and the whole was concentrated to less than 340 c.c., and diluted to exactly that volume with boiling water, the volume being read when the solution was as near as possible at boiling temperature. All the solutions were started in this way, and all solutions, not of the same volume, were of this concentration. The size of the crystals decided upon as desirable for quantitative work was a length varying from 20 to 30 m.m. The ratio of the volume of solution to the horizontal surface of the containing crystallising dish is identical with the depth of solution, and so for each volume a dish was selected which would give a constant depth. A depth of about 6 m.m. was found to give ample space between crystals 20 to 30 m.m. long, formed from a solution of the strength indicated; and in so shallow a solution there is the added advantage that the crystals, when first formed on the surface, fall to the bottom directly without slant. The diameter of the dish, which will hold 340 c.c. at a depth of 6.3 m.m., is 26 c.m., and, in general, the diameter for this depth is the square root of twice the contained volume.

From the previous discussion it will be seen that with a given volume and concentration, and with the size of the dish determined, the size of the crystals will depend upon the number of crystal points first started in the solution as it cools beyond the point of saturation, and that the number of these points depends upon the conditions which obtain in the crystallising dish during the time of supersaturation, and only then. Of course one can escape the uncertainty of accident by providing in such a solution a sufficient number of minute, clean crystals to supply nuclei for crystallisation, but these should be so small as not materially to increase the concentration. A difficulty

would arise in this method of procedure in that the temperature would have to be chosen so low that the little crystals would not dissolve in the hot solution before growth began, and also so high that the cold crystals would not locally chill the surface of the solution below the saturation-point, and thus start crystallisation in a fine powder throughout the whole mass. For the volume and concentration above indicated, about fifty such points would be necessary to give crystals of 30 m.m. in length.

The method used in this work for starting the proper number of crystal points is one which, with a little practice on the part of the experimenter, works satisfactorily—how much so will be seen from the second part of this paper. When the hot measured solution is poured into the crystallising dish, the latter is carefully covered to prevent further concentration, dust, or surface chilling, and is allowed from eight to ten minutes to cool, when a slight blast of air (the air being filtered through cotton), under pressure equivalent to 12 m.m. of mercury, is blown upon the surface, and the latter is watched closely for the first minute crystals which (formed before the colder blast), float out upon the surface. When the proper number of these crystals for the volume and concentration are not only formed but persist in the hot solution, the blast is quickly removed, and the crystals are allowed to grow while the dish is covered and left undisturbed at constant temperature, usually over night. As the number of crystals always bears the same relation to the surface exposed, one watches not for a certain number of crystals but rather for a certain spacing, constant for each experiment, which it is easy to approximate each time.

Successive Crystallisations.

In the experiments mentioned above, 171 grms. of clean copper sulphate crystals were dissolved in acidified water, and concentrated to 340 c.c. On crystallisation at 23° C., 275 c.c. of mother-liquor and 78 grms. of crystals were obtained. It was desired to evaporate further the 275 c.c. of concentrated solution to the same strength as the 340 c.c. of the original solution—a concentration which will always give the ratio of 78 grms. of crystals to 275 c.c. of mother-liquor. It was calculated* that to this end any saturated solution of copper sulphate must be evaporated to 67.1 per cent of its volume, and that this will then give a mother-liquor equal to 54.3 per cent, and a crystal weight equal to 15.4 per cent of the same volume.

Based upon this calculation, a model has been constructed which is found in Table I., below. According to this table, each mother-liquor is to be concentrated to 67.1 per cent of its volume, and from it is to be obtained a weight of crystals, and a volume of new mother-liquor in the ratio of 28+ grms. to 100 c.c. Table II. contains the results of the first attempt to follow this model. By comparing these tables, it will be seen that the point of concentration indicated in the second column of Table I. was not reached exactly in any case, but the important column VI. of Table II. shows that the size of crystals has fallen each time within the desired limits of from 20 to 30 m.m. in length.

It should be said concerning the figures in columns I. to IV. that it is very difficult to measure quickly solutions which are held as closely as possible to the boiling temperature, and that an approximation to the model was all that was necessary, since large variations do not appreciably affect the results in column VI., which contains the results especially sought.

When the solution gets as small as 58 c.c., the nuclei may be supplied by introducing minute crystals—as only ten are needed in this case—but these crystals must first

* The calculation is as follows:— $275 : 78 = 100 : 28.3$. Solubility at 23° = 21.7 grms. CuSO_4 sp. gr. of solution being 1.214; $21.7 \text{ grms. CuSO}_4 = 33.8 \text{ grms. CuSO}_4 \cdot 5\text{H}_2\text{O}$. Required, $0.238 \text{ V} = 0.283 \text{ V}$, or mother-liquor, $\text{V}' = 54.3$ per cent V . Then the original solution at point of saturation at 23° must have measured $275 \div 0.543 = 506.4$ c.c.; $340 \div 506.4 = 67.1$ per cent, evaporating ratio; $0.283 \times 0.543 = 15.4$ per cent, ratio of crystal weight to saturated solution.

TABLE I.—Model.

Process number.	I. Solution saturated at 25°. Each volume = 54.3 per cent of precursor.	II. Solution evaporated to 67.1 per cent of volume in I.	III. Weight of crystals = 15.4 per cent of volume in I.	IV. Ratio of weight of crystals to volume in I.	V. Diameter of crystal- lising dish to give solution in II. a depth of 6+ m.m. $D = \sqrt[3]{\frac{V}{\pi}}$	VI. Size of crystals.
1.	C.c. [506.4 calculated]	C.c. 340			$\sqrt[3]{680} = 26$	
	275		78	0.283		
2.	275 149	184	42	0.282	$\sqrt[3]{369} = 19$	
3.	149 81	100	23	0.284	$\sqrt[3]{200} = 14$	
4.	81 44	54	12.5	0.284	$\sqrt[3]{109} = 10.5$	

TABLE II.

I.	II.	III.	IV.	V.	VI.
1.	x	340			
	275		78	0.283	25
2.	275 157	190	39	0.248	20
3.	157 85	105	25	0.294	13.5
4.	85 50	58	12+	0.24	9.6

be washed with hot water, and must then be large enough to exist in the hot solution. In larger solutions the method described is better.

Should one desire to form crystals of a different size, a little practice would be necessary to determine the proper conditions of spacing for that size, and the formula for the size of the crystallising dish would be somewhat changed. It would then be possible to prepare crystals of any desired size not only from the original solution but from all the successive mother-liquors.—*American Chemical Journal*, xxv., No. 5.

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 35).

Examination of the Blank Sodic Solution.

13. The amount of the alumina extracted by the sodic solution being appreciable though small, and the amount of sodic solution used being large, it was desirable to make similar experiments on the sodic solution itself. Taking the same amount of sodic solution (20 grms. of crystallised sodium carbonate and 2½ grms. of caustic soda), as was used in the last analysis, the following numbers were obtained:—

SiO₂ 0.0049.

Fe₂O₃, Al₂O₃, SiO₂ 0.0009 (the alumina and silica being probably inappreciable).

CaO 0.0005.

CaO 0.0019, due to action on the porcelain dish.

Mg₂P₂O₇ nil.

Undecomposed Material : Specific Gravity.

14. The material left undecomposed by the acid and sodic solutions was white in colour, but there was admixed with it a little black material of higher specific gravity than that of the silicate; the black material was found to be chromite. The specific gravity of the admixture was determined from 1.2831 grms. of the material by means of a 3 c.c. pycnometer. The usual corrections for the temperature of the water and for the displaced air being made, it was found that the weight of the material which occupies a c.c. at 17° C. is 3.171 grms.

Undecomposed Material : Chemical Analysis.

15. 0.8981 grm. of the undecomposed material was fused with mixed potassium and sodium carbonates. There was a perceptible action on the platinum crucible involving the eventual separation of a little platinum from the magnesium pyrophosphate, but otherwise not interfering with the analysis. The chromite was partially decomposed, and the chromium which passed into solution manifested itself by the green colour of the oxides after the iron had been removed from the ignited precipitate by the Deville-Cooke method; the oxides of iron, aluminium, and chromium had been twice precipitated together in dilute solution by the sodium acetate method, and finally with ammonia; they were thus free from magnesium.

The following numbers were obtained:—

SiO₂ + chromite 0.5056.

Chromite, after treatment with HF and H₂SO₄, 0.0027.

Fe₂O₃, Cr₂O₃, Al₂O₃, SiO₂ 0.1545; of this 0.1201 yielded Cr₂O₃, Al₂O₃, SiO₂ 0.0393, which itself on being analysed gave Cr₂O₃ 0.0054, Al₂O₃ 0.0314, SiO₂ 0.0006, the loss being probably Al₂O₃.

MnS 0.0042.

CaO 0.0369 (a double precipitation with ammonium oxalate).

Mg₂P₂O₇ 0.5384.

16. *Alkalis.*—0.4994 grm. of the undecomposed material, analysed by the Lawrence Smith method, gave:—Sodium and potassium chlorides 0.0183; K₂PtCl₆ (free from filter) 0.0079; adherent to filter and ignited 0.0025. During the operation the chromite was, partially at least, converted into chromate, and Cr₂O₃ 0.0018 was separated from the alkaline solution before the mixed chlorides could be weighed.

Undecomposed Material : Action of Hydrochloric Acid and Sodic Solution.

17. It is well known that the residue from the treatment with hydrochloric acid and sodic solution is far from insensible to the action of those reagents; it became desirable to ascertain the amount of this action under similar circumstances to those of the analyses of the unattracted material itself.

1.10388 grms. of the undecomposed material were therefore treated in the same way as the unattracted material. The following numbers were obtained:—
a. Residual material.—Part washed from filter, 0.8807; part adherent to filter and ignited, 0.0363.

b. The acid solution yielded:—

Fe₂O₃, Al₂O₃, SiO₂ 0.0150; of this 0.0080 gave Al₂O₃ 0.0005, and SiO₂ nil.

SiO₂ 0.0022 was obtained from the solution, and is a measure of the action on the vessels.

CaO 0.0076.

After decomposition of the ammonium chloride by nitric acid, SiO₂ 0.0033 and Fe₂O₃, Al₂O₃ 0.0008 were separated from the solution, and were due to the action of the nitric acid on the porcelain dish.

Mg₂P₂O₇ 0.0649.

c. The sodic solution yielded:—

SiO₂, with trace of undecomposed material, 0.0763.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

After treatment with HF and H_2SO_4 and subsequent ignition, 0.0014.

Fe_2O_3 , Al_2O_3 , SiO_2 0.0071; of this 0.0060 gave Al_2O_3 , SiO_2 0.0052, and the latter when analysed gave Al_2O_3 0.0048 and SiO_2 nil.

CaO 0.0028.

(Further CaO 0.0016, due to action of nitric acid on the porcelain dish).

$\text{Mg}_2\text{P}_2\text{O}_7$ nil.

Undecomposed Material: Effect of Ignition.

18. As the undecomposed material contains a considerable proportion of ferrous oxide, it was probable that ignition would appreciably increase its weight. It is necessary to determine the amount of this action, for that part of the silicate which is adherent to the filter cannot be weighed until after ignition.

0.0332 grm. of the undecomposed material, after ignition with the gas blowpipe, became 0.0331; there was thus no appreciable change of weight, the increase of weight by oxidation being neutralised by loss due to volatilisation.

Undecomposed Material: Effect of Hydrofluoric and Sulphuric Acids followed by Ignition.

19. Similarly, it is necessary to determine the effect of hydrofluoric and sulphuric acids, followed by ignition, in order to determine for each case the amount of the finely divided silicate which has passed through the pores of the filter and is admixed with the silica. It was found that 0.0696 grm. of the undecomposed material gave after this treatment a residue which weighed 0.0572.

Action of Nitric Acid on the Porcelain.

20. For the precipitation of the small amount of calcium it is necessary to add to the solution enough ammonium oxalate to convert not merely the calcium itself, but also the magnesium, into oxalate, otherwise part of the calcium may remain in solution. The large amount of ammoniacal salt thus introduced has to be removed before the precipitation of the magnesium; if this is effected by evaporation and ignition, there is great danger of loss through spurring; if it is effected by evaporation with strong nitric acid, there is an appreciable action on the porcelain dish and the magnesium precipitate is not quite pure. The amount of action depends on the duration of the evaporation with nitric acid and on the amount of the latter; it will thus vary in different experiments. To gain some idea of the amount of the action, the silica and calcium thus brought into solution were on several occasions determined and have been recorded above:—

SiO_2 0.0061 (§ 11), 0.0067 (§ 12).

CaO 0.0036 (§ 4), 0.0040 (§ 9), 0.0020 (§ 10), 0.0013 (§ 11), 0.0022 (§ 11), 0.0012 (§ 12).

The mean of the numbers for the CaO is 0.0024; the weight of the corresponding $\text{Ca}_2\text{P}_2\text{O}_7$ would be 0.0054; this amount may therefore be properly subtracted from the determined weight of the $\text{Mg}_2\text{P}_2\text{O}_7$ when the amount of nitric acid used has been about the average.

(To be continued).

THE RATE OF NITRIFICATION OF SOME FERTILISERS.*

By W. A. WITHERS and G. S. FRAPS.

THE value of any fertiliser depends on its availability to the plant; that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms, viz., (1) free nitrogen, (2) as certain organic compounds, (3) as ammonium salts, (4) as nitrates.

* Contribution from the North Carolina Agricultural Experiment Station. From the *Journal of the American Chemical Society*, xxiii, No. 5.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the leguminosæ, which includes clover, peas, beans, the peanut, vetch, &c.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin, asparagin, and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All nitrogenous organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, water-melons, corn, common sorrel, and other plants seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and still others nitrogen in the form of ammonia; nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites, and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, &c., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilisers which cannot be utilised directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilisers.

This is the object of the work which will be described in the following pages.

Historical.

Müntz and Girard (*Central-Blatt Agr. Chem.*, 1891, xx., 656, Abs.) have determined the relative rate of nitrification of some fertilisers. A small quantity of the fertiliser was intimately mixed with natural soil, and kept at the temperature of 15–25° C., properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was thirty, thirty-two, and thirty-nine days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:—

	Nitrified in thirty days. Per cent.	Recovered by corn. Per cent.
Ammonium sulphate..	75.0	76.7
Dried blood..	72.4	55.0
Roasted horn, fine	71.0	60.1
Flesh meal	70.4	—
Horn trimmings, fine	55.5	53.3
Poudrette, rather coarse	18.1	14.9
Roasted leather, fine..	11.6	38.3
Leather chips, raw	0.4	—

In another series, the order of nitrification was as follows:—Bat guano, dried grasshoppers, dried cockchafer, flesh meal, dried blood (the substance nitrified to the greatest extent being given first). There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from Joinville (used in the experiment referred to above), then in a garden soil, then in a chalky soil, then in a marled moor soil. Very little nitrification occurred in a very calcareous clay, except with cow manure, and yellow lupins, which loosened their texture; and none in an acid moor soil with the same two exceptions.

P. Bonâme (*Expt. Station Record*, ix., 732, Abs.) determined the nitrates in the drainage water from a sandy soil deficient in lime to which fertilisers had been added. The order of nitrification at the end of the first month was found to be—fish guano (most rapid), blood, fertiliser, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate (see Table I.).

TABLE I.

Nitrate Nitrogen in 100 grms. Soil (in m.grms.).

Soil	One month.	Two months.	Three months.
Soil	4.2	5.0	5.0
Soil and ammonium sulphate.	22	29	35
Soil and dried blood	66	74	85
Soil and oil cake	59	82	95
Soil and fish guano	74	110	113
Soil and calcium carbonate ..	6.2	7.3	6.0
Soil, calcium carbonate, and ammonium sulphate	75	133	186
Soil, calcium carbonate, and dried blood	123	151	159
Soil, calcium carbonate, and oil cake	97	139	137

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances. At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from organic materials.

Experimental.

Effect of Dilution of Soil.—The effect of ratio of soil to fertiliser was studied in some preliminary experiments. 3000 grms. of a sandy soil from a pasture, which had been sifted through a 6-mesh sieve, was mixed well with the quantity of dried blood containing 1.0, 0.5, 0.25 grm. nitrogen, and the mixtures placed in a dark closet for fourteen days. They were watered at suitable intervals, endeavouring to maintain the original 10 per cent of water. The temperature was about 27° C. The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann-Schulze method. Results are given in Table II.

TABLE II.

Dilution.	Nitrates. Grm.	Nitrified. Per cent.
Soil	—	0.0963
Soil and 1.0 grm. nitrogen	1/3000	0.4564
Soil and 0.5 grm. nitrogen	1/6000	0.3626
Soil, 0.5 grm. nitrogen, and 1.785 grm. calcium carbonate	—	0.5043
Soil and 0.25 grm. nitrogen	1/12000	0.2354

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertiliser. Assuming that the mean weight of a cubic foot of soil is 80 pounds, and that the soil is cultivated to the depth of 6 inches, then the dilution of the nitrogen applied as a fertiliser is 1/57000, which is much greater than in any of the above cases. But it must be remembered that a fertiliser is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertiliser is probably much less than 1/12000. This would be particularly true with materials like dried blood, which are insoluble in water. Soluble fertilisers, like ammonium sulphate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil must be a very slow process.

(To be continued.)

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—There should be no difficulty in getting red-lead free from carbonates. A red-lead which gives 1 per cent of carbon, equal to about 3.6 per cent of carbonic acid, or, in other words, consisting of white-lead to the extent of one-third, is well described as of the "worse" (with the accent on the last syllable) kinds. Possibly had your correspondent shown the sample to his paint friends they would have told him that the sample did not consist of red-lead at all, but was a barytes dyed with a coal-tar colour, and that his 1 per cent carbon came mostly from the latter. The market is flooded with such rubbish; some firms getting weekly bulky consignments of barytes from the Continent for this and similar purposes (*vide* Custom House returns). Orange lead, made by furnacing white-lead, must not be confounded with red-lead made by furnacing litharge, although any one outside the paint trade might not be able to differentiate by mere sight between them any more than he would between the sophisticated article just referred to and the genuine red-lead. The orange lead, however, effervesces when treated with dilute acetic acid. *Red-lead should not.* Orange lead at the most contains not more than 6 per cent of undecomposed carbonate. It is therefore ridiculous to say that there is any red-lead whatever on the market which has carbonate to the extent of one-third. But why use red-lead at all? Commercial nitrate of lead and "bichrome" are almost chemically pure, and may be had quite cheap from any drysalter. Why therefore cannot the steel-works chemist make his own chromate of lead by mutual decomposition of the above in the proportion of two equivalents of nitrate of lead 660 parts, to one equivalent of bichrome 295 parts, wash thoroughly with distilled water, and dry completely? He would thus have a genuine chrome-yellow—far superior to anything he would be likely to meet with in commerce or get from "pure" chemical dealers.

His "blanks" would thus be reduced to a minimum. His reagents would be, like Cæsar's wife, above suspicion. Many dealers in "pure" chemicals free from so-and-so get them from paint, &c., manufacturers who know nothing about them and care less. They are supposed to be makers, but sell them as they buy them. How any chemist worthy of the name can be satisfied with mere "blank" determinations as the only test of their reagents passes my comprehension. Do they not make a qualitative examination of them at the least, or make a determination on a sample containing a known percentage of carbon? The reagent has a certain work to do besides yielding a greater or less result in a blank experiment. The following hints may be of use in testing:—Genuine red-lead gives no effervescence with dilute acetic acid, cedes nothing to ammoniated alcohol, and is completely soluble in dilute nitric acid plus oxalic acid. Genuine chromate of lead cedes nothing to ammoniated alcohol, dissolves instantaneously in a large excess of potash, and is re-precipitated by acetic acid.

Nitric acid, concentrated or dilute, in the hot or in the cold, has no action whatever on genuine peroxide of lead, but dissolves it instantly on the addition of oxalic acid and water if the concentrated acid has been used. The writer would not put himself to the trouble of performing a blank experiment on any of these three substances which did not fulfil the requirements of these and other tests, and would reject them even if the blank were completely negative, as not being what they were represented to be, and therefore presumably unfit for the purpose for which they were intended.—I am, &c.,

J. G. MCINTOSH.

London, E.

DR. JERWITZ'S FAT-EXTRACTION APPARATUS.

To the Editor of the Chemical News.

SIR,—An illustrated description of the above apparatus was recently given in the CHEMICAL NEWS (vol. lxxxi., p. 229). As, however, its somewhat complicated and fragile appearance may possibly operate against its adoption by technical chemists and analysts engaged in the estimation of fats, it may interest your readers to know that Dr. Jerwitz's apparatus has been exclusively used in this laboratory during the past twelve months with the most satisfactory results.

The extractor and condenser being in one piece, there are no troublesome cork or mercury joints to attend to, and the extractor being joined to one side of the condenser, the sample can be placed in position ready for extraction, by simply removing and replacing a ground glass stopper, the apparatus itself, once fixed in position on a stand, or against a wall, never requiring to be disturbed. Used in conjunction with a capacious water-bath, the temperature of which is controlled by a thermo-regulator, and with a constant supply of cold water for condensing, the apparatus is perfectly automatic in its action, and requires absolutely no attention during the extraction. It is so simple and reliable in operation that it only requires to be known to be widely adopted.—I am, &c.,

WILLIAM W. MELLON.

Laboratory,
81, Rogerson's Quay, Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 1, July 1, 1901.

Chemical Equilibrium. Phosphoric Acid and the Chlorides of the Alkaline Earths.—M. Berthelot.—From the observations and experiments described in this paper, it may be apparently shown that the relation between a molecule of phosphoric acid in combination and an equivalent number of alkaline earth bases, which combine to saturate this molecule in the phosphate precipitates, vary from two to four equivalents, according to the nature and the relative proportions between the bodies placed in contact, the free or combined acids or bases, alkaline earth chlorides, &c. These variations are always a function of the time elapsed since the beginning of the reaction.

New Treatment of Niobite. Preparation and Properties of Fused Niobium.—Henri Moissan.—By means of the electric furnace it is easy to obtain a mixture of niobium and tantalum. From this mixture, by applying Marignac's method, the niobium and tantalum can be separated and obtained in the form of oxide. Niobic acid, which was absolutely non-reducible by means of carbon at the highest temperature of an ordinary furnace, can be reduced in the electric furnace, and gives a compact mass of the metal, which is very hard and contains a very small quantity of combined carbon. This mass is solid at the fusing-point of platinum; it is only attacked by acids with great difficulty, and has no action on water-vapour at a red heat, but burns in oxygen with ease, producing a stable acid; it possesses at the same time very curious reducing properties. These various properties seem to separate niobium from the metals and bring it closer to the simple non-metals boron and silicon.

Acidimetry of Arsenic Acid.—A. Astruc and J. Tarbouriech.—The saturation of arsenic and phosphoric acid by the alkaline bases seems to be very similar in its action. On the contrary, it differs in several points when

saturation is effected with the alkaline-earth bases; in particular, the tri-metallic salt obtained in cold dilute solution by arsenic acid in presence of the alkali and excess of a chloride of an alkaline earth. This is transformed into a di-metallic salt, from which the excess of base is saturated by the acid used for titration. This latter reaction does not take place with phosphoric acid.

A Colourless Compound of Sodium Tetrazotolylsulphite with Ethyl-β-naphthylamine and its Transformation into a Colouring-matter.—A. Seyewetz and M. Blanc.—Sodium sulphite gives, with the di- and tetrazoic derivatives, compounds in which the properties characteristic of diazoic bodies are masked—which, in fact, do not give colouring-matters with the amines and phenols. If, however, the sulphite derivative, when added to the amine or the phenol, is left exposed to light, the colouring-matter is produced. The authors investigate the mechanism of this reaction, and examine the colouring-matters produced in each case.

Action of Benzoic Aldehyde on Sodium Menthhol, and New Methods of Preparation of Benzylidene Menthone.—C. Martine.—The author's experiments apparently show—(1) That sodium menthol behaves in the same manner as borneol with regard to benzoic aldehyde, and it gives with this substance benzylidene menthone; (2) the reaction takes place probably according to the equation given by Claisen; (3) the benzylidene menthone can also be obtained by treating sodium menthone with benzoic aldehyde.

Union of Camphor with β-Oxy-α-naphthoic Aldehyde.—André Helbronner.—Haller has shown that camphor is susceptible of uniting with a certain number of aromatic aldehydes to give perfectly definite crystalline compounds corresponding to the formula $C_8H_4 \begin{matrix} C=CH-R \\ | \\ CO \end{matrix}$.

It is interesting to discover that an analogous compound can be produced with β-oxy-α-naphthoic aldehyde. The author was not able to experiment with the aldehyde itself. Indeed, the sodium of sodium-camphor would give the sodium compound, on account of the hydrogen in the OH-group. However, good results were obtained by working with the ether-oxides of this aldehyde.

Action of Bromacetophenone on Sodium Acetylacetone.—Fr. March.—The author obtains a triacetone of the type $(CH_3-CO)_2=CH-CH_2-CO-CH_3$ by acting with bromacetophenone on sodium acetylacetone. The action apparently takes place according to the equation—

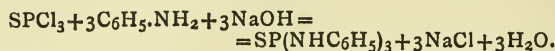
$$(CH_3-CO)_2=CHNa + CH_2Br-CO-C_6H_5 =$$

$$= NaBr + (CH_3-CO)_2=CH-CH_2-CO-C_6H_5.$$

MISCELLANEOUS.

Pocket-Book of Electrical Engineering Formulæ.—The second edition of Geipel and Kilgour's "Pocket-Book of Electrical Engineering Formulæ" is just issued by The Electrician Publishing Company, London, price 7s. 6d. nett. The authors, who both occupy a prominent position in the electrical industry, and are in close touch with the latest practice in all matters relating to the applications of electricity to industrial purposes, have carefully revised and added to the matter which forms the chief contents of the book. Electric Traction, the Transmission of Electric Power, and the many other subjects which, since the first publication of the Pocket-Book, have come prominently to the front, have been given special attention, with the result that the book contains over 850 pages. The use of a thin, hard paper, and a compact binding has enabled the Publisher to reduce the bulk of the work, which is, notwithstanding the mass of matter crowded between the covers, not too large for the pocket. The electrical engineer engaged in practical everyday work will find the Pocket-Book of great service.

Action of Sulphochloride of Phosphorus on the Aromatic Amines in the Presence of an Alkali.—W. Autenrieth and P. Rudolph.—The authors have attempted to react on the aromatic amines with sulphochloride of phosphorus in the presence of an alkali, and they have observed that the reaction proceeds as with the oxychloride of phosphorus. In this reaction neutral derivatives of the orthosulphophosphoric acids of the general formula $SP(NHR)_2$ are very easily obtained, and these crystallise very well. In much less quantity they obtained disubstituted sulphophosphoric acids of the formula $SP(NH.R)_2OH$. These latter, which crystallise with difficulty and are not very stable, have not been examined very closely; the authors have been content to examine the principal product which is formed according to the equation—



The authors also describe, in the same paper, the derivatives obtained by the "sulphophosphorylation" of aniline, of *p*-toluidine, and of *p*-phenitidine.—*Berichte*, vol. xxxiii., p. 2112.

VICTORIA UNIVERSITY.

The OWENS COLLEGE, MANCHESTER.

CHEMISTRY COURSE.

Full particulars of this Course, qualifying for the VICTORIA UNIVERSITY DEGREES in Chemistry and the College Technological Chemistry Certificate, will be forwarded on application.

The SESSION commences on OCTOBER 1st.

S. CHAFFERS, Registrar.

UNIVERSITY OF BIRMINGHAM.

FACULTIES OF SCIENCE AND ARTS.

1901-2.

The SESSION will commence on TUESDAY, OCTOBER 1st, 1901.

The UNIVERSITY confers DEGREES in SCIENCE (including ENGINEERING) and in ARTS upon Students who have attended prescribed University Courses of Study. These Courses are also open to all who may wish to join them, whether Candidates for Degrees or not.

EXHIBITIONS, SCHOLARSHIPS, PRIZES, &c., are offered for competition.

DIPLOMAS in EDUCATION are granted to Candidates fulfilling the required conditions.

SPECIAL TECHNICAL COURSES are provided in Engineering (Civil, Mechanical, and Electrical), Metallurgy, Applied Geology, and in Malting and Brewing.

For the present, the University also provides PRELIMINARY COURSES in preparation for the MATRICULATION EXAMINATION of the University, and for other purposes.

SYLLABUSES of the Faculties of Science and Arts, and of the School of Malting and Brewing, are now ready, and may be obtained gratis from Messrs. CORNISH, New Street, Birmingham, or on application at the University.

There is also a Faculty of Medicine (including a Department of Dentistry). A Syllabus containing full particulars is published separately.

THE

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 30th; Lectures begin October 8th, 1901.

Hostels for Men and for Women Students.

Prospectuses on application to the SECRETARY.

BIRKBECK INSTITUTION,

Breams Buildings, Chancery Lane, E.C.

LECTURES AND PRACTICAL WORK in—

CHEMISTRY .. J. E. MACKENZIE, Ph.D., D.Sc.

PHYSICS A. GRIFFITHS, D.Sc.

METALLURGY.. G. PATCHIN, A.R.S.M.

DAY CLASSES.—

CHEMISTRY—Tuesday, Thursday, Saturday, 10—1.

PHYSICS—Monday, Wednesday, Friday, 2.30—5.30.

METALLURGY—Monday, Wednesday, Friday, 10—1.

EVENING CLASSES in all subjects.—

Every Evening except Saturday, from 6 p.m.

INSTRUCTION IN

PURE CULTIVATION OF YEAST, According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactories, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

GENUINE WORKING RECIPES,

IN THE

OIL, GREASE, SOAP, PAINT, COLOUR,
VARNISH, and ALLIED TRADES.

Latest Up-to-date Processes and Methods—English and Continental Household and Trade Specialities, in every line. (Many Unpatented).

Consultations—Correspondence by Letter.

Analysis—Samples Matched—Identicals Found—Samples and Articles Received for Testing and Analysis—Certificates Given—Contract Work Undertaken.

WRITE FOR FULL LIST, FREE.

E. SCOTT,

Practical Chemist, Analyst, and Expert.

168, Church Street, NORTH SHIELDS.

ACETONE.

JOHS. OSWALDOWSKI,
ALTONA, near HAMBURG.

THE CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

Edited by SIR WILLIAM CROOKES, F.R.S.

Published every Friday. Price 4d. Annual Subscription post free, including Indices, £1.

CHARGES FOR ADVERTISEMENTS.

	s.	d.
Five lines in column (about 10 words to a line)	0	5 6
Each additional line	..	.. 0 6
Whole column	..	.. 1 15 0
Whole page	..	.. 3 0 0

A reduction made for a series of insertions.

Cheques and Post-Office Orders, crossed "London and County Bank," payable to the order of Sir William Crookes

6 & 7, CREED LANE, LUDGATE HILL, LONDON,
E.C.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2175.

THE NADIR OF TEMPERATURE, AND ALLIED PROBLEMS.*

- I. PHYSICAL PROPERTIES OF LIQUID AND SOLID HYDROGEN. 2. SEPARATION OF FREE HYDROGEN AND OTHER GASES FROM AIR. 3. ELECTRIC RESISTANCE THERMOMETRY AT THE BOILING-POINT OF HYDROGEN. 4. EXPERIMENTS ON THE LIQUEFACTION OF HELIUM AT THE MELTING-POINT OF HYDROGEN. 5. PYROELECTRICITY, PHOSPHORESCENCE, &c.

By JAMES DEWAR, LL.D., D.Sc., F.R.S., &c.

DETAILS are given in this paper which have led to the following results:—

The helium thermometer which records $20\cdot5^{\circ}$ absolute as the boiling-point of hydrogen, gives as the melting-point 16° absolute. This value does not differ greatly from the value previously deduced from the use of hydrogen gas thermometers, viz., $16\cdot7^{\circ}$. The lowest temperature recorded by gas thermometry is $14\cdot5^{\circ}$, but with more complete isolation and a lower pressure of exhaustion, it will be possible to reach about 13° absolute, which is the lowest temperature that can be commanded by the use of solid hydrogen. Until the experiments are repeated with a helium gas thermometer filled at different pressures, with the gas previously purified by cooling to the lowest temperature that can be reached by the use of solid hydrogen, no more accurate values can be deduced.

The latent heat of liquid hydrogen about the boiling-point as deduced from the vapour pressures and helium-thermometer temperatures, is about 200 units, and the latent heat of solid hydrogen is about 16 units.

The order of the specific heat of liquid hydrogen has been determined by observing the percentage of liquid that has to be quickly evaporated under exhaustion in order to reduce the temperature to the melting-point of hydrogen, the vacuum vessel in which the experiment is made being immersed in liquid air. It was found that in the case of hydrogen the amount that had to be evaporated was 15 per cent. This value along with the latent heat of evaporation, gives an average specific heat of the liquid between freezing- and boiling-point of about 6. When liquid nitrogen was similarly treated for comparison, the resulting specific heat of the liquid came out $0\cdot43$, or about 6 per atom. Hydrogen therefore follows the law of Dulong and Petit, and has the greatest specific heat of any known substance.

The same fine tube used in water, liquid air, and liquid hydrogen gave respectively the capillary ascents of $15\cdot5$, 2, and $5\cdot5$ divisions. The relative surface tension of water, liquid air, and liquid hydrogen are therefore in the proportion of $15\cdot5$, 2, $0\cdot4$. In other words, the surface tension of hydrogen at its boiling-point is about one-fifth that of liquid air under similar conditions. It does not exceed one thirty-fifth part the surface tension of water at the ordinary temperature.

The refractive index of liquid hydrogen determined by measuring the relative difference of focus for a parallel beam of light sent through a spherical vacuum vessel filled in succession with water, liquid oxygen, and liquid hydrogen, gave the value $1\cdot12$. The theoretical value of the liquid refractive index is $1\cdot11$ at the boiling-point of the liquid. This result is sufficient to show that hydrogen, like oxygen and nitrogen in the liquid condition, has a refractivity in accordance with theory.

Free hydrogen, helium, and neon have been separated

from air by two methods. The one depends on the use of liquid hydrogen to boil the dissolved gases out of air kept at a temperature near the melting-point of nitrogen; the other on a simple arrangement for keeping the more volatile gases from getting into solution after separation by partial exhaustion. By the latter mode of working something like $1/34000$ th of the volume of the air liquefied appears as uncondensed gas. The latter method is only a qualitative one for the recognition and separation of a part of the hydrogen in air. In a former paper on the "Liquefaction of Air and the Detection of Impurities" (*Chem. Soc. Proc.*, 1897), it was shown that 100 c.c. of liquid air could dissolve 20 c.c. of hydrogen at the same temperature. The crude gas separated from air by the second method gave on analysis—hydrogen 32·5 per cent, nitrogen 8 per cent, helium, neon, &c., 60 per cent. After removing the hydrogen and nitrogen the neon can be solidified by cooling in liquid hydrogen and the more volatile portions separated.

There exists in air a gaseous material that may be separated without the liquefaction of the air. For this purpose air has to be sucked through a spiral tube filled with glass-wool immersed in liquid air. After a considerable quantity of air has been passed, the spiral is exhausted at the low temperature of the liquid air-bath. The spiral tube is now removed, and allowed to heat up to the ordinary temperature, and the condensed gas taken out by the pump. After purification by spectroscopic fractionation, the gas filled into vacuum tubes gives the chief lines of xenon. The spectroscopic examination of the material will be dealt with in a separate paper by Professor Liveing and myself. A similar experiment made with liquid air kept under exhaustion, the air current allowed to circulate being under a pressure less than the saturation pressure of the liquid to prevent liquefaction, resulted in krypton being deposited along with the xenon.

A study of fifteen electric resistance thermometers as far as the boiling-point of hydrogen has been made, and the results reduced by the Callendar and Dickson methods. The following table gives the results for seven thermometers, viz., two of platinum, one of gold, silver, copper, and iron, and one of platinum-rhodium alloy. It will be noted that the lowest boiling-point for hydrogen was given by the gold thermometer. Next to it came one of the platinum thermometers, and then silver, while copper and the iron differ from the gold value by 26 and 32 degrees respectively. The gold thermometer would make the boiling-point $23\cdot5^{\circ}$ instead of the $20\cdot5^{\circ}$ given by the gas thermometer. Then the reduction of temperature under exhaustion amounts to only 1° instead of 4° as given by the gas thermometer. The extraordinary reduction in resistance of some of the metals at the boiling-point of hydrogen is very remarkable. Thus copper has only $1/105$ th, gold $1/30$ th, platinum $1/35$ th to $1/17$ th, silver $1/24$ th the resistance at melting ice, whereas iron is only reduced to $1/8$ th part of the same initial resistance. The real law correlating electric resistance and temperature within the limits we are considering is unknown, and no thermometer of this kind can be relied on for giving accurate temperatures up to and below the boiling-point of hydrogen. The curves are discussed in the paper, and I am indebted to Mr. J. H. D. Dickson and Mr. J. E. Petavel for help in this part of the work.

Helium separated from the gas of the King's Well, Bath, and purified by passing through a U-tube immersed in liquid hydrogen, was filled directly into the ordinary form of Cailletet gas receiver used with his apparatus, and subjected to a pressure of 80 atmospheres, while a portion of the narrow part of the glass tube was immersed in liquid hydrogen. On sudden expansion from this pressure to atmospheric pressure a mist from the production of some solid body was clearly visible. After several compressions and expansions, the end of the tube contained a small amount of a solid body that passed directly into gas when the liquid hydrogen was removed, and the tube kept in the vapour of hydrogen above the liquid. On

* Abstract of the Bakerian Lecture read before the Royal Society, June 13, 1901.

Electrical Resistance Thermometry at the Boiling-point of Hydrogen.

	Metals.	Platinum (P ₁).	Potassium (P ₂₇).	Alloy platinum rhodium (Pt-Rh ₂₀).	Gold (Au ₄₀).	Silver (Ag ₄₃).	Copper (Cu ₄₇).	Iron (Fe ₂₈).
R ₁		4.2050	39.655	36.87	16.10	8.336	11.572	4.290
R ₀		3.1037	28.851	31.93	11.58	5.990	8.117	2.765
Resistance at CO ₂		—	19.620	—	—	—	—	—
"	liq. O	0.9473	7.662	22.17	3.380	1.669	1.589	0.633
"	liq. N	—	—	—	—	—	1.149	—
"	liq. Ox	—	4.634	20.73	—	—	—	—
"	liq. H	0.183	0.826	18.96	0.381	0.244	0.077	0.356
"	liq. Hx	—	0.705	18.90	0.298	0.226	0.071	—
α		0.003548	0.003745	0.003607	0.003903	0.003917	0.004257	0.005515
Ω' = - $\frac{I}{a}$		-281.81	-267.04	-646.37	-256.19	-255.33	-234.93	-181.31
T. observed o liq. O (°C.)		-182.5	-182.34	-182.4	-182.37	-182.41	-182.41	-182.85
δ		2.5797	2.6767	4.7447	-0.18448	0.34553	1.2676	-8.3238
Calculated temp. (°C.)—								
At CO ₂		—	-81.48	—	—	—	—	—
"	liq. O	-182.505	-182.342	-282.401	-182.37	-182.41	-182.413	-182.855*
"	liq. N	-182.601	-181.60	-163.51	-182.4	-182.41	-183.320	-182.850†
"	liq. Ox	—	-207.12	-207.87	—	—	-194.42	—
"	liq. H	-243.61	-206.55	-208.99	—	—	-195.22	—
"	liq. Hx	-243.13	-237.88	-238.73	-249.37	-242.06	-223.54	-213.82*
"	liq. Hx	—	-237.55	-239.75	-249.5	-242.06	-223.99	-210.29†
"	liq. Hx	—	-238.85	-239.77	-251.23	-242.84	-223.70	—
Ω		-258.00	-238.48	-240.78	-251.1	-242.82	-224.15	—
"		-257.28	-244.50	-543.39	-257.90	-252.26	-225.62	-258.40*
"		—	-244.15	-530.32	-257.8	-252.25	-226.04	-246.80†
Ratio	$\frac{R_0}{\text{Res. at B.P. of H.}}$	16.96	34.93	1.684	30.39	24.55	105.41	7.767

R₁, R₀, are the resistances at 100° C. and 0° C. respectively. The remaining resistances are clear from the table.

α means that the liquid is boiling under exhaustion measured by about 30 m.m. of mercury.

Ω' is the temperature, in degrees of the metal in question, at which the resistance would vanish.

Ω is the temperature Centigrade at which the resistance would vanish, either on the Callendar or on the Dickson method.

Calculated temperatures—the upper, Callendar's method; the lower by Dickson's.

Callendar's α and δ are calculated from the given values of R₁, R₀, the resistance of liquid O, and the temperature observed in liquid O.

The same data are used to calculate the Dickson formula, except in the cases of P₁, whose formula is given in the *Phil. Mag.*, June, 1898; P₇, whose formula is given in *Roy. Soc. Proc.*, vol. lxiv., p. 228; and Pt-Rh₂₉, Arg₃₂, and Cu₄₇, which were calculated by least squares.

* Callendar.

† Dickson.

lowering the temperature of the liquid hydrogen by exhaustion to its melting-point, which is about 16° absolute, and repeating the expansions on the gas from which the solid had separated by the previous expansions at the boiling-point or 20.5°, *no mist was seen*. From this it appears the mist was caused by some other material than helium, in all probability neon, and when the latter is removed no mist is seen, when the gas is expanded from 80 to 100 atmospheres, even although the tube is surrounded with solid hydrogen. From experiments made on hydrogen that had been similarly purified like the helium and used in the same apparatus, it appears a mist can be seen in hydrogen (under the same conditions of expansion as applied to the helium sample of gas), when the initial temperature of the expanding gas was twice the critical temperature, but it was not visible when the initial temperature was about two and a-half times the critical temperature. This experience applied to interpret the helium experiments, would make the critical temperature of the gas under 0° absolute.

Olzewski in his experiments expanded helium from about seven times the critical temperature under a pressure of 125 atmospheres. If the temperature is calculated from the adiabatic expansion starting at 21° absolute, an effective expansion of only 20 to 1 would reach 6.3°, and 10 to 1 or 8.3°. It is now safe to say, helium has been

really cooled to 9° or 10° absolute without any appearance of liquefaction. There is one point, however, that must be considered, and that is the small refractivity of helium as compared to hydrogen, which, as Lord Rayleigh has shown, is not more than one-fourth the latter gas. Now as the liquid refractivities are substantially in the same ratio as the gaseous refractivities in the case of hydrogen and oxygen, and the refractive index of liquid hydrogen is about 1.12, then the value for liquid helium should be about 1.03, both taken at their respective boiling-points. In other words, liquid helium at its boiling-point would have a refractive index of about the same value as liquid hydrogen at its critical point, and as a consequence, small drops of liquid helium forming in the gas near its critical point would be far more difficult to see than in the case of hydrogen similarly situated.

The hope of being able to liquefy helium, which would appear to have a boiling-point of about 5° absolute, or one-fourth that of liquid hydrogen, is dependent on subjecting helium to the same process that succeeds with hydrogen; only instead of using liquid air under exhaustion as the primary cooling agent, liquid hydrogen under exhaustion must be employed, and the resulting liquid collected in vacuum vessels surrounded with liquid hydrogen. The following table embodies the results of experience and theory:—

	Initial tem- perature.	Critical tem- perature.	Boiling- points.
Liquid helium? ..	5°?	2°?	1°?
Solid hydrogen ..	15	6	4
Liquid " ..	20	8	5 (He?)
Exhausted liquid air ..	75	30	20 (H)
52°C. ..	325	130	86 (Air)
Low red heat ..	760	304	195 (CO ₂)

The first column gives the initial temperature before continuous expansion through a regenerator, the second the critical point of the gas that can be liquefied under such conditions, and the third the boiling-point of the resulting liquid. It will be seen that by the use of liquid or solid hydrogen as a cooling agent we ought to be able to liquefy a body having a critical point of about 6° to 8° absolute, and boiling-point of about 4° or 5° absolute. Then, if liquid helium could be produced with the probable boiling-point of 5° absolute this substance would not enable us to reach the zero of temperature; another gas must be found that is as much more volatile than helium as it is than hydrogen in order to reach within 1° of the zero of temperature. If the helium group comprises a substance having the atomic weight 2, or half that of helium, such a gas would bring us nearer the desired goal. In the meantime the production of liquid helium is a difficult and expensive enough problem to occupy the scientific world for many a day.

A number of miscellaneous observations have been made in the course of this inquiry, among which the following may be mentioned. Thus the great increase of phosphorescence in the case of organic bodies cooled to the boiling-point of hydrogen under light stimulation is very marked, when compared with the same effects brought about by the use of liquid air. A body like sulphide of zinc cooled to 21° absolute, and exposed to light, shows brilliant phosphorescence on the temperature being allowed to rise. Bodies like radium that exhibit self-luminosity in the dark, cooled in liquid hydrogen maintain their luminosity unimpaired. Photographic action is still active although it is reduced to about half the intensity it bears at the temperature of liquid air. Some crystals when placed in liquid hydrogen become for a time self luminous, on account of the high electric stimulation brought about by the cooling causing actual electric discharges between the crystal molecules. This is very marked with some platino-cyanides and nitrate of uranium. Even cooling such crystals to the temperature of liquid air is sufficient to develop marked electrical and luminous effects.

Considering that both liquid hydrogen and air are highly insulating liquids, the fact of electric discharges taking place under such conditions proves that the electric potential generated by the cooling must be very high. When the cooled crystal is taken out of either liquid and allowed to increase in temperature, the luminosity and electric discharges take place again during the return to the normal temperature. A crystal of nitrate of uranium gets so highly charged electrically that, although its density is 2.8, and that of liquid air about 1, it refuses to sink, sticking to the side of the vacuum vessel and requiring a marked pull on a silk thread, to which it is attached, to displace it. Such a crystal rapidly removes cloudiness from liquid air by attracting all the suspended particles on to its surface. The study of pyro-electricity at low temperatures will solve some very important problems.

During this inquiry I have had the hearty co-operation of Mr. Robert Lennox, to whom my thanks are due, and Mr. J. W. Heath has also given valuable assistance.

The Accumulator Industries, Limited, beg to notify that their registered offices have been transferred to the works premises at Maybury, Woking, Surrey. The London offices remain as heretofore, 14, Silver Street, Bloomsbury, W.C.

ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA.*

By G. D. LIVEING, M.A., Sc.D., F.R.S.,
Professor of Chemistry in the University of Cambridge,

and
JAMES DEWAR, M.A., LL.D., F.R.S.,
Fullerian Professor of Chemistry, Royal Institution, London.

(Concluded from p. 38).

THE pressure p , of a gas G, above the same material in the liquid state, at temperature T, is given approximately by the formula—

$$\log p = A - \frac{B}{T},$$

where A and B are constants for the same material. For some other gas G' the formula will be—

$$\log p_1 = A_1 - \frac{B_1}{T},$$

and—

$$\log \frac{p}{p_1} = A - A_1 + \frac{B_1 - B}{T}.$$

Now for argon, krypton, and xenon respectively the values of A are 6.782, 6.972, and 6.963, and those of B are 339, 496.3, and 569.2; so that for these substances, and many others, $A - A_1$ is always a small quantity, while—

$$\frac{B_1 - B}{T}$$

is considerable, and increases as T diminishes. Hence the ratio of p to p_1 increases rapidly as T diminishes, and by evaporating all the gases from the solid state, and keeping the solid at as low a temperature as possible, the gas first removable at the lowest pressure consists in by far the greatest part of that which has the lowest boiling-point, which in this case is nitrogen, and is succeeded, with comparative abruptness, by the gas which has the next higher boiling-point. In this way the nitrogen and oxygen are removed without the necessity of sparking or absorption. The change from one gas to another is easily detected by examining the spectrum in the sparking tube, and the reservoirs into which the gases are pumped can be changed when the spectrum changes, and the fractions separately stored. Or, if several sparking tubes are interposed in such a way as to form parallel communications between the tubes b and c , any one of them can be sealed off at any desired stage of the fractionation.

The variation of the spectra of both xenon and krypton with variation in the character of the electric discharge is very striking, and has already been the subject of remark, in the case of krypton, by Runge, who has compared krypton with argon in its sensitiveness to changes in the electric discharge. Runge distinguishes krypton rays which are visible without a jar and those which are only visible with a jar discharge. The difference in the intensity of certain rays, according as the discharge is continuous or oscillatory, is no doubt very marked, but, with rare exceptions, we have found that the rays which are intensified by the oscillatory discharge can be seen with a continuous discharge when the slit of the spectroscopic is wide. Runge used a grating, whereas we have, for the sake of more light, used a prism spectroscopic throughout, and were therefore able to observe many more rays than he.

There is one remarkable change in the xenon spectrum produced by the introduction of a jar into the circuit. Without the jar xenon gives two bright green rays at about λ 4917 and λ 4924, but on putting a jar into the circuit they are replaced by a single still stronger ray at about λ 4922.† In no other case have we noticed a change so striking as this on merely changing the

* A Paper read before the Royal Society, June 20, 1901.

† This line is almost identical with a strong helium line, but the yellow line of helium was not seen.

character of the discharge. Changes of the spectrum by the introduction of a jar into the circuit are, however, the rule rather than the exception, and there are changes in the spectrum of krypton which seem to depend on other circumstances. In the course of our examination of many tubes filled with krypton in the manner above indicated, we have found some of them to give with no jar the green ray λ 5571, the yellow ray λ 5871, and the red ray λ 7600 very bright, while other rays are very few, and those few barely visible. Putting a jar into the circuit makes very little difference; the three rays above mentioned remain much the brightest, nearly, though not quite, so bright as before, and the blue rays, so conspicuous in other tubes, though strengthened by the use of the jar, are still very weak. In other tubes the extreme red ray is invisible, the rays at λ 5571 and 5871 absolutely, as well as relatively, much feebler, while the strong blue rays are bright, even brighter than the green and yellow rays above named. In one tube the blue rays could be seen, though not the other. This looks very much as if two different gases were involved, but we have not been able to assure ourselves of that. The case seems nearly parallel with that of hydrogen. There are some hydrogen tubes which show the second spectrum of hydrogen very bright, and others which show only the first spectrum; the second spectrum is enfeebled or extinguished by introducing a jar into the circuit, while the first spectrum is strengthened; and the conditions which determine the appearance of the ultra-violet series of hydrogen rays have not yet been satisfactorily made out.

It is to be noted that putting the jar out of circuit does not in general immediately reduce the brightness of the rays which are strengthened by the jar discharge. Their intensity fades gradually, and is generally revived, more or less, by reversing the direction of the current, but this revival gets less marked at each reversal until the intensity reaches its minimum. The rays strengthened by the jar discharge also sometimes appear bright, without a jar, on first passing the spark when the electrodes are cold, and fade when the electrodes get hot, reappearing when the tube has cooled again. Moreover, if the discharge be continued without a jar, the resistance in the krypton tubes increases rather rapidly, the tube becomes much less luminous, and finally refuses to pass the spark. With an oscillatory discharge the passage of the spark and the brightness of the rays are much more persistent. This seems to point to some action at the electrodes, which is more marked in the case of krypton than in that of xenon.

The wave-lengths of the xenon and krypton rays in the accompanying tables were determined, in the visible part of the spectrum, with a spectroscope having three white flint-glass prisms of 60° each, by reference to the spark spectrum of iron, except in the cases of the extreme red ray of krypton, which was referred to the flame spectrum of potassium, and its fainter neighbour, which we saw but did not measure. The indigo, violet, and ultra-violet rays were measured in photographs, taken with quartz lenses and two calcite prisms of 60° each. The spectrum of the iron spark was photographed at the same time as that of the tube, the former being admitted through one-half of the slit, and the latter through the other half.

The xenon spectrum is characterised by a group of four conspicuous orange rays of about equal intensities, a group of very bright green rays of which two are especially conspicuous, and several very bright blue rays. The only list of xenon rays we have seen is that published by Erdmann, with which our list does not present any close agreement except as to the strongest green lines. The number of xenon rays we have observed is very considerable, and some of them lie very near to rays of the second spectrum of hydrogen, but inasmuch as these rays are more conspicuous with a jar in circuit than without, which is not the character of the second spectrum of hydrogen, and, moreover, many of the brightest of the hydrogen rays are absent from the spectrum of the tubes, we conclude that these rays are not due to hydrogen.

Certain rays, which we have tabulated separately, have been as yet observed in only one tube; they include a very strong ultra-violet ray of unknown origin, and one either due to some substance other than xenon, or to some condition of the tube which has not been repeated in the other tubes.

Our krypton rays agree much more closely with Runge's list, but outnumber his very considerably, as might be expected when prisms were used instead of a grating. Prisms, of course, cannot compete with gratings in the accuracy of wave-length determinations. We think that the krypton used by Runge must have contained some xenon, and that the rays for which he gives the wave-lengths 5419'38, 5292'37, and 4844'58 were really due to xenon, as they are three of the strongest rays emitted by our xenon tubes, and are weak in, and in some cases absent from, the spectra of our krypton tubes.

Tables of the Approximate Wave-lengths of Xenon and Krypton Rays.

Rays observed only with a Leyden jar in circuit have an * prefixed, those observed only when no Leyden jar was in circuit have a † prefixed.

The intensities indicated are approximately those of the rays when a jar is in circuit, except in the case of the two rays to which a † is prefixed, which are not seen when a jar is in circuit. Rays which are equally intense whether a jar is in circuit or not have a || prefixed to the number indicating their intensities; those which are less intense with a jar than without have a < prefixed to the number expressing their intensities. The rest are, in general, decidedly more intense with a jar than without.

Xenon Rays.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
*5596	4	5439	3
* 14	1	20	10
6472	1	5372	6
6358	1	* 68	1
45	3	39	6
20	1	13	1
02	1	09	1
6278	3	5292	10
71	3	62	2
6183	1	60	2
81	1	40	—
66	1	27	1
6097	6	02	1
51	6	5192	6
36	5	89	3
5976	6	85	3
72	—	79	3
46	2	26	3
35	<1	23	1
06	1	07	3
5895	1	5080	2
76	1	68	5
56	1	52	1
25	2	45	6
17	—	25	<1
5777	4	4988	4
59	4	72	2
51	5	† 24	†4
27	4	* 22	8
20	4	† 17	†4
00	6	4890	3
5668	4	87	—
60	1	84	4
17	—	83	—
09	1	76	4
5583	1	44	10
73	1	30	1
32	4	23	3
5473	3	* 18	3
61	3	07	<1
* 51	1	4793	1

Wave-lengths.	Intensity.
4787	2
79	2
69	2
40	I
34	<I
31	I
23	I
14	I
4698	3
4677	Band to of close lines.
4668	
52	
34	4
24	2
16	<2
02	3
4592	8
86	3
77	5
56	3
45	2
41	3
35	3
25	2
22	5
00	I
4486	I
81	I
71	5
62	2
49	10
40	6
34	I
15	2
07	8
4396	3
93	4
86	4
75	3
69	4
56	4
43	I
37	I
31	3
22	10
11	3
4297	3
86	3
72	3
69	3
63	3
51	2
45	3
39	10
27	8
23	I
15	5
14	10
09	6
04	8
01	I
4198	I
93	6
81	10
76	I
72	I
63	3
59	3
46	3
42	I
32	2
21	I
12	2
09	6

Wave-lengths.	Intensity.
4106	3
00	2
4099	3
93	I
79	<I
74	I
60	I
58	6
50	6
44	I
43	I
37	6
29	I
25	3
21	I
02	3
3994	2
91	3
86	I
81	I
75	I
73	2
57	I
55	4
51	<6
44	3
39	I
26	I
23	6
15	I
08	4
06	I
03	I
3894	3
85	3
80	3
77	3
70	2
62	2
58	2
55	I
50	2
49	I
42	4
29	I
26	I
24	I
15	I
11	3
07	I
01	I
3792	I
87	I
83	I
81	6
76	3
73	I
70	I
66	I
63	2
62	I
57	I
46	3
37	I
31	2
21	3
17	2
12	2
08	I
3689	I
77	3
73	2
64	I
62	2
58	I

Wave-lengths.	Intensity.
3655	2
50	I
45	6
41	2
32	2
24	10
16	I
13	4
10	2
07	4
02	I
3597	3
84	8

Wave-lengths.	Intensity.
3580	8
65	4
56	3
53	5
43	6
23	4
10	2
04	I
01	4
3468	2
61	I
54	I

Wave-lengths of Rays of Unknown Origin observed in the Spectrum of one Tube containing Xenon but not present in the Spectrum of other Tubes.

Wave-length.	Intensity.	Wave-length.	Intensity.
4589	—	3890	I
4071	I	72	I
67	I	3797	5
63	—	41	4
11	I	3684	10
3998	I	3573	2

Krypton Rays.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
7600	8	5186	I
7587	2	72	I
6771	I	66	5
6578	I	43	4
42	3	26	6
11	2	5087	3
6487	3	78	I
58	<I	73	2
51	3	57	3
20	<4	34	I
6305	3	23	4
6170	2	14	2
6095	I	4980	I
82	I	60	I
56	2	46	I
21	I	03	2
11	2	4847	2
5992	3	45	2
5873	I	33	5
71	<10	26	3
5771	2	12	3
53	2	4766	10
5690	5	63	3
82	5	39	10
50	I	4694	3
32	2	80	5
5571	<10	59	8
63	3	50	I
53	I	35	6
44	I	20	8
23	2	15	6
06	2	10	3
00	2	4598	I
5483	I	93	2
46	2	83	4
29	I	77	8
24	I	25	3
03	I	05	2
5319	I	4490	2
05	I	75	6
5278	I	64	3 pair
29	I	54	I
18	I	37	6
15	I	32	6
* 09	5	23	2
03	I	00	I

* This is taken from Runge's number for the wave-length, omitting the fraction.

Wave-length.	Intensity.	Wave-length.	Intensity.
4387	3	3862	1
76	3	59	1
63	2	58	1
56	12	47	1
23	2	44	2
20	118	42	1
19	113	39	1
18	3	37	2
01	7	17	2
4293	10	06	2
83	113	05	3
74	114	3784	10
69	3	79	8
60	1	72	4
56	1	59	2
51	5	55	6
37	4	46	6
4185	3	42	6
72	1	36	3
45	8	34	4
40	2	22	5
19	3	19	10
09	6	15	1
4099	8	3691	1
89	8	87	5
65	7	81	7
58	6	70	7
45	4	67	1
38	2	64	3
08	2	61	3
05	1	54	10
3997	3	49	3
94	6	38	4
88	2	32	10
65	1	24	1
55	2	08	6
39	1	00	6
28	3	3590	3
21	8	74	1
18	2	54	2
13	6	45	6
07	6	03	2
01	1	3489	2
3896	3	70	1
76	7	60	3

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 41).

Development of the Latent Image.—Of all the developers that I have tried, the pyrogallic-soda developer has been most satisfactory.

Freshly-prepared plates can take equal parts of both solutions without the addition of water usual for dry plates. For raising the intensity of the negative, which is usually low in the beginning, a water solution of potash (1:3) may be used, being added to the developer in amount from a few drops to half the volume of soda. A few drops of potassium bromide (1:10) render the plate transparent and cause a rise of intensity. It must be remembered that potassium bromide considerably retards the appearance of the picture, and that it only acts with full power when it is present from the beginning of development. Potassium bromide added during the development is nearly without action.

Cold developer acts similarly to potassium bromide. The warmer the former is, the sooner and more complete is the appearance of the image, while very cold solutions lead to negatives richer in contrast.

* *Annalen der Physik*, 1901, vol. v.

I prefer to start developing with the bath as cold as possible, and warm it as soon as the most active lines have appeared. I manage the warming in the simplest manner—by rubbing the bottom of the bath with the flat of the hand, which gains the desired effect without trouble. In many cases very clear and powerful negatives are produced with a bath very rich in potassium bromide, followed by a second containing no potassium bromide after the first lines have appeared.

I proceed otherwise when dealing with single exceedingly fine lines, or with dense groups of lines differing but slightly in energy. In this case I make a preliminary exposure with a very narrow slit, from 0.001 m.m. downwards. If this does not suffice, which is generally the case, I repeat it, changing the time of development to correspond to the desired result—sometimes shortening, sometimes lengthening it. If the second operation is not successful, a third will generally suffice. It is advisable to expose for a sufficiently long time, but in no case to carry the development further after the lines have appeared. For the analysis of extensive spectra with large energy differences this method is useless, because the slit aperture of the collimator, which is of necessity narrow, considerably enhances the most powerful lines, in which rays of very different activity occur in contiguity, and singles them out before the weaker lines have attained the capacity for development.

Older plates can seldom bear developing with undiluted solutions without becoming fogged. For these, it is necessary to add water (1 volume pyrogallol, 1 volume soda, 1 to 2 volumes water), as well as to increase the quantity of potassium bromide (1 to 3 drops of 1:10 potassium bromide per c.c. undiluted pyro-soda solution). Prescriptions for general use cannot here be given. The composition of the developer must be regulated each time by the nature of the experiment and by the age of the plate.

The development takes place with fresh plates, and without potassium bromide in the developer, in two to three minutes, with potassium bromide in three to four minutes, while it requires twice or three times as long with plates one to two months old, on account of the necessarily weaker solutions and the increase in potassium bromide.

I develop small plates (13 × 37 m.m.) in an evaporating dish, pouring the mixed solution directly on to the plate. It is advisable to transfer the wet plate from one bath to the other with suitable tongs, on account of the fragile nature of the film. I use tongs with hooked ends of hard indiarubber, which clip the plate at the edges. It is best to leave plate and pincers joined together until the negative is dry.

The appearance of the picture is seen on a white foundation better than on a coloured, and in the same way white dishes are preferable to all others.

The illumination of the dark room may be the same as that for the ordinary dry plate. I always work with the brown light, which is photographically more inactive than the red, and soft to the eyes, which cannot be said of the other.

Fixing, Washing, and Drying.—When development is finished, the basin containing the negative is filled up several times with water, and the plate then immersed in a solution of sodium hyposulphite (1:3 to 1:4), in which the silver bromide dissolves in a few seconds. In an acid fixing-bath the solution takes longer. In the short period of fixing, the ultra-violet plate differs advantageously from the ordinary dry plate. Productions of lasting value are better preserved by dipping for a few seconds in a second fixing-bath after rinsing the surface with water. In order to wash out the fixing, the plate is placed for about two minutes upright in a stream of water—not so strong as to spoil the film—then sprayed carefully with distilled water, and finally supported on a platform, free from dust, in such a manner that the water can all drain off at one corner. The washing may be conducted in standing water instead of flowing; this is to be recommended in the case

of large sizes. I use for this purpose suitable beakers and evaporating basins. If the film is placed downwards, it is fully washed in ten to fifteen minutes with four or five changes of water. It is freed from its soluble salts, on account of its thinness, more readily than the ordinary dry plate. Drying requires ten to fifteen minutes in the fairly warm still air of the room.

It is not necessary to treat every plate with the care above described, but it is essential when the greatest purity is required. In general, where little dry-spots are no disadvantage, the process can be made much shorter. The plate, after being removed from the first fixing-bath, is held for two minutes in a stream of water and then dried in the neighbourhood of a stove (not too hot), over a lamp or near its cylinder, for which a few minutes suffices.

The Dry Negative.—The image is grey-brown, in transmitted light black-grey with a transparent ground. This transparency makes the deposition of dust particles much more noticeable than with other negatives, which always have a thick ground.

A spectrum on the ultra-violet-sensitive plate may be very greatly enlarged, on account of the extraordinary fineness of its lines. The spectra obtained from a very narrow slit give clear pictures enlarged a hundred times. The ordinary dry plate cannot bear enlargement to such an extent, the reason for which can only lie in the greater thickness (five times) and in the relatively greater proportion of gelatin in the sensitive film.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF NITROCELLULOSE.*

By G. LUNGE and J. BEBIE.

(Continued from p. 42).

A. Influence of Water upon the Process of Nitration (continued).

WITH 16.6 per cent water (experiment 5), we get a completely soluble product, and with this arrive at the group of the collodion cottons. The action of the water becomes increasingly more intense; there is a rapid decrease of the nitrogen percentage with increase of the water percentage from 18 per cent onwards. The group of soluble nitrocelluloses between 170 and 196 c.c. is bounded with a difference of water content of only 4 per cent, and this through the interval of about 16.5—20.5 per cent. Between experiment 7 and 8 lies octonitrocellulose of commercial importance (typical collodion cotton), with a nitrogen content of 177.2 c.c. By reference to the curve (of which the ordinates give c.c. NO per 1 grm., and abscissæ water percentage of the nitration mixture), the corresponding water content should be 19.5 per cent. This was confirmed by experiment, for a nitration mixture containing 19.42 per cent water led to the desired stage of nitration, which is always to be obtained in this manner.

We must now turn to the communications published by Wyss-Naef on the manufacture of cotton-silk at Besançon. According to this the collodion cotton is produced by treating cellulose for four to six hours with a mixture of 85 parts sulphuric acid, and 15 parts fuming nitric acid. Concentrated sulphuric is not expressly mentioned, but only that can be intended as mention is afterwards made of the great attraction for water of the nitration mixture. Again, a technical method exists for reasons of economy, that if, in a mixture of acids, one of the acids is concentrated, and the other must be diluted to a certain extent, one should use the dearer nitric acid in the concentrated form, but the cheaper sulphuric in the dilute form. But the specific gravity of the nitric acid is given as 1.52; hence for sulphuric acid we must understand concentrated acid.

These statements are revised in the book, "The Artificial Silk," recently published by Dr. Süvern. But Lunge and Weintraub were not able to obtain collodion cotton in this manner. The body prepared by them according to the prescription of Wyss-Naef contained only 19 per cent of soluble matter, and moreover nitration was not complete, for by means of the polarisation microscope unchanged cellulose was seen. The nitration was carried out at the temperature of the room. But we have since ascertained that nitration is conducted at a somewhat higher temperature in the art-silk manufacture. As the sulphuric acid is present in great excess it was not ascertained that this acid mixture would lead to materially different results on raising the temperature. Hence, some experiments were made in this direction for the completion of those of Lunge and Weintraub, but, as is shown by the following table, with equal ill-success:—

Temp.	Time of nitration.	C.c. NO per 1 grm.	Solubility.	Increase.
30°	4 hours	199.89	17.14	160.2
40°	7 hours	209.20	15.54	143.1

The nitration products obtained are only soluble to a small degree, but here, on the contrary, the nitration is complete in contrast to nitration at the ordinary temperature. The cellulose remained unchanged. In polarised light the fibres appeared light steel-blue.

In the above-named communications the nitration is characterised as complete when all the fibres reflect blue. But it must be added that nitrocelluloses with a nitrogen content below 190 c.c. (and these are they which come into consideration here), never showed a blue illumination. The statements of Wyss-Naef must also be taken with caution.

We now return to the discussion of the first series of experiments. If the nitrogen content falls below 160 c.c. the solubility again decreases. The nitration stages from hexanitrocellulose (C₂₄...) downwards are insoluble in ether-alcohol. This agrees with the statements of Vieille, in contradiction, however, with those of Eder, according to whom di- and tri-nitrocellulose (C₁₂...) were soluble. Eder obtains these products by treating cellulose with very hot acid mixtures. But in this the cellulose molecule does not remain intact, which is evident from the fact that, from the dinitrate thus produced, no cellulose can be regenerated with ferric chloride. With a water content of about 25 per cent and upwards nitration is not further completed after twenty-four hours' reaction. For example, in experiment 12 the acid mixture was kept on the cellulose for three days; but there always remained some unconverted cellulose. By the method of Lunge and Weintraub the amount of this comes out at 4.1 per cent. Calculated from material freed from cellulose the nitrogen content was 108.12 c.c., which would correspond to tetra-nitrocellulose. But (for reasons to be mentioned later), the nitrogen determination cannot be exact in this case, and hence the figures must only be regarded as an approximation.

With a further increase of water the nitration effect is very slight. At first there is still something of this, but afterwards the products which result have the properties of oxycellulose; they are completely or partially soluble in dilute alkalis, and can be recovered from the solution by acids or alcohol; they become deeply coloured with basic colour agents, reduce Fehling's solution, and form phenylhydrazine compounds.

As already remarked, the time of nitration during these experiments lasted twenty-four hours, and the temperature was that of the room.

For producing collodion cotton on a large scale a raised temperature was adopted in most cases. This is in general advantageous, because it increases the speed of reaction. A few experiments, carried out at a higher temperature and a correspondingly shorter time of nitration, showed that the results of the last series of experiments are directly related to these nitration conditions.

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

The following table shows the results obtained with the acid mixture used in experiment 7:—

Expt.	Time of nitration. Hours.	Temper- ature.	C.c. NO per 1 gm.	Solubility in ether-alcohol.	Increase.
1.	4	17°	183'54	95'60	155'1
2.	24	17°	184'78	99'81	156'2
3.	4	40°	183'40	99'58	148'1
4.	4	60°	172'48	99'82	52
5.	4	60°	182'80	99'71	146'7

With this nitration mixture, even at the temperature of the room, nitration was complete after four hours (Expt. 1). The product is of greater increase than that produced at 40°; on the other hand, the solubility in ether-alcohol is less easy and complete. By raising the temperature to 60° partial denitration quickly set in. After four hours' reaction the nitrogen content sank to 172'48 c.c. In this experiment the structure of the cotton was entirely destroyed; hence the fine fibrous pulp was, for the purpose of washing, poured, together with the acid mixture, into a great quantity of cold water, after which the nitration product was treated in the usual way. The increase rapidly diminished. Secondary reactions set in through the hot acid mixtures. Experiment 5 shows that a higher nitration is next effected, in which the time of nitration was confined to a quarter of an hour; therefore a partial denitration again takes place through the action of the hot acid mixtures. Hence the conditions of this experiment yield the product in the shortest time. But the nitrocelluloses produced at so high a temperature are said not to give collodion capable of being spun (as we learn from a private communication of Dr. Brönner), and are hence useless for the purposes of the artificial silk manufacture. The structure of the cotton suffers a great change on nitration with increasing water content of the acid mixtures. It remained almost unchanged up to the proportion of about 15 per cent water; from about 18 per cent onwards the fibres appeared somewhat drawn together. With higher percentages of water the structure became almost entirely destroyed; the fibres break up into small particles, and become matted into clotted masses. This destructive action reaches its maximum with 23—25 per cent. It is these compact products that offer greater resistance to the action of sulphuric acid, on account of the small amount of surface. With more dilute acid mixtures the fibres remain intact, and are only split into smaller fragments on longer treatment.

This series of experiments gives us an idea of the great importance of the proportion of water contained in the nitration mixtures.

(To be continued).

ON THE CIRCULATION OF SALT AND ITS BEARING ON CHEMICO-GEOLOGICAL PROBLEMS.

By WILLIAM ACKROYD, F.I.C., F.C.S.,
Public Analyst for Halifax.

THE few observers who have practically gone into the question of chlorine distribution in the British Isles are aware that only isolated facts are on record; that we have not that fulness of information which could be utilised in constructing iso-chlors; that the chlorine in rainfall, more particularly in the neighbourhood of towns, is wildly variable, and has been studied in only a few cases, and therefore that it is a mistake for Prof. Joly to say we possess "very full information" on any one of these points. It is also a mistake, arising from hasty reading perhaps, for him to impute to me the style of reasoning which he gives in the sixth paragraph of his communication (CHEM. NEWS, vol. lxxxi., p. 301); this is based on a misunderstanding of the method I have devised of arriving at the ratio of earth-salt to sea salt in river waters.

May I add for Prof. Joly's information that it is assumed all the combined chlorine is equally diffused throughout the limestone, and that for every degree of hardness acquired by the water a proportionate amount of combined chlorine enters into solution; at the same time silica, alumina, and organic matter, &c., will be taken up either in solution or suspension. Let us leave Craven.

On Combined Chlorine as a Measure of Solvent Denudation.

No less remarkable results are obtained by turning to other regions. I will take another example, and let it be noted that this instance refers to some 13,300 square miles of the earth's surface, a somewhat larger sample than part of the watershed of the Aire.

The waters of Connecticut and Massachusetts contain combined chlorine; the element has been derived either in whole or part from the rock bed over and through which the water passes, or in whole or part from the rain. Now the rocks, whether felspar, serpentine, or dolomite, collected by the U.S. Geological Survey from Blandford, Middlefield, Granville, Rowe, Russel, Chester, and over a score of other places, contain no chlorine (see *Bull. U.S. Geol. Survey*, No. 148). Therefore the chlorine must have descended with the rains. The gradual increase in the iso-chlor figures as the sea-coast is approached is a final demonstration of the marine origin of the chlorine. Let it then be noted that, deduct what we may from the chlorine figure for any water in these regions, and what is left is still representative in the largest degree possible of cyclic sea-salt. Herein I take it lies the fallacy of Prof. Joly's calculation on p. 302, where he deducts 0.1 per 100,000 as "the average amount of chlorine carried by rains to the rivers after evaporation" from 0.3 parts per 100,000, "the amount of chlorine appearing in the mean river water." I may also be permitted to point out a discrepancy which must be a source of confusion to those who are trying to get at the root of the matter. In the *B. A. Report* for 1900, p. 721, we are told "the proportion of Na in Prof. Joly's average river water is only 5.73 per million." The chlorine equivalent of this is 0.88 part per 100,000. From 0.3 to 0.88 is a difference of nearly 266 per cent. One turns in vain to Appendix I., p. 65 (*Trans. Roy. Dub. Soc.*, 1899), for enlightenment on the matter.

Now as chlorine is the most important of all the elements combined together in the substances forming the dissolved matters of the ocean, it would be legitimate, if it were possible, to take the chlorine contents of the ocean and divide by the annual chlorine increment yielded by the rivers, after all necessary corrections, to get at the age of the earth. Mr. Millard Reade has used calcium sulphate; Prof. Joly, sodium; then why not chlorine? It will have become abundantly clear by now that in using chlorine on the assumption of uniformity of the work of solvent denudation our divisor would be relatively so small as compared with the numerator as to give a quotient too large to obtain scientific credence. The example just given is striking proof of this, and, however liberal one may appear to be in an allowance for salt transported from the sea and back again, the needs of the case do not seem to be adequately met. Much mathematical discretion may be exercised in fixing this allowance, for while 50 per cent does not much impair results, 70 per cent begins to make them look bad, and things are going worse out of all proportion when 90 per cent has been wrung out of an unwilling opponent.

Evaporation.

In further considering the possibility of using a chlorine divisor it would be necessary to very particularly consider those parts of the earth's surface, by no means inextensive, where rivers rise in or flow through the torrid zone. The excessive evaporation must be taken into account. In the case of the Nile I have already pointed out that there is a variation of something like 400 per cent in the

chlorine figure, and other rivers like the Niger and Congo must similarly vary. Has Prof. Joly made allowance for these seasonal variations? And did Sir John Murray in sampling his average river waters provide fully for them? Because it goes without saying that, as chlorine combined with sodium forms the great constituent of the ocean, the latter element must share in these restrictions to a very important degree.

The Great Storm of 1839.

The public interest aroused in the subject of salt circulation by my paper has led to many reminiscences being communicated to me. One to the effect that early in 1839 the window-panes in this town, facing west, were *thickly* encrusted with salt during a storm has been confirmed by reference to contemporary records. An account of the storm is given in a book entitled "A Narrative of the Dreadful Disasters occasioned by the Hurricane which visited Liverpool and Various Parts of the Kingdom on the Nights of Sunday and Monday, January 6th and 7th, 1839." It is a reprint from the pages of the *Liverpool Mercury*. The following are the passages confirming local verbal narrative:—

"It is a singular fact that trees about Huddersfield during the storm on Monday appeared as if covered with hoar-frost, but as it did not freeze it led to an examination, when it turned out that this was a briny deposit which the wind had probably brought from the Irish Sea."

Under the heading "Longton" (near Preston?) there is this passage, "Twelve o'clock at noon, wind W. The trees and hedges appear as covered with hoar-frost by reason of particles of salt."

On the Origin of the Saltiness of the Dead Sea.

Storm effects like these enable one to realise that with extreme meteorological conditions, such as have admittedly obtained in the past history of the Jordan watershed, it may have been no uncommon thing for Palestine to be drenched with sea-salt by the prevalent westerly gales, in which case a more important contribution towards the saltiness of the Dead Sea would be made than could be furnished by the widely distributed limestone rocks. The quieter circulation of salt which is in progress in calmer times would probably contribute a no less important share.

Prof. Joly raises no valid objection to such a theory when he points out that wide differences exist in the composition of the waters of salt lakes; indeed it would be strange if there did not! Each case must be studied in connection with its supposed causes. No good can come, at the present stage of the inquiry, of comparing the Dead Sea with the Great Salt Lake; such a comparison is illogical. To confine one's attention to the former I have shown that the ratio of the closely related ions Cl and Br is practically the same for the Dead Sea and the Mediterranean, and such a comparison was made because it appeared not unlikely that whatever vicissitudes one of the waters might have suffered, two such elements on account of their close kinship would be likely to preserve their proportions if the salts of one of the waters were derived either altogether or very largely from the other. The vicissitudes referred to are suggested by the question, Would the wind borne salts of the Mediterranean, brought down by rain and lodged in a locality of higher evaporation, undergo a concentration which would tend in time to a "salting out" or precipitation of some of the dissolved bodies, and the production of a "mother-liquor" similar to the waters of the Dead Sea? From what we know of the history of such mixed solutions we are entitled to answer in the affirmative. In the manufacture of bay salt from Mediterranean sea-water the bittern bears interesting points of resemblance to Dead Sea water, and no doubt some individuality has been superadded to the latter by its limestone gathering grounds.

Several other matters arise in Prof. Joly's criticism which I think will be fully answered by a thoughtful repudiation of my original paper.

THE RATE OF NITRIFICATION OF SOME FERTILISERS.*

By W. A. WITHERS and G. S. FRAPS.

(Concluded from p. 46).

Rate of Nitrification.

THE experiments to determine the relative rate of nitrification were carried out as follows:—The fertilising materials were those sent out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (6 meshes to the inch), and a quantity of material equivalent to 0.6 gm. nitrogen was intimately mixed with 1000 grms. of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to raise the percentage from 6.3 to 11.6 per cent. At suitable periods, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was 28–30° C., and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertiliser if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann-Schulz method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in Table III.

On account of the surprisingly small percentage of ammonium sulphate nitrified in the first series, the experiments with cotton-seed meal and ammonium sulphate were repeated, the time being twenty-six days, the temperature 23–26° C., and the sample moistened as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0.1641 gm. nitrogen as nitric acid per kilogram., whereas the former contained only 0.0595 gm.

Rate of Nitrification and Availability of Nitrogen.

We have selected, and give below (Table III.), the results obtained by vegetation tests with oats and Hungarian grass by Jenkins and Britton (*Conn. State Station Report*, 1897, 357), and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method, and the neutral permanganate method, the materials being those used in these nitrification experiments.

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cotton-seed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilisers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18.9 per cent in three weeks, and only 21.7 per cent in six weeks.

Effect of Calcium Carbonate.

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cotton-seed meal, 162; dried fish 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II.), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually

* Contribution from the North Carolina Agricultural Experiment Station. From the *Journal of the American Chemical Society*, xxiii., No. 5.

TABLE III.

Rate of nitrification.						Availability.				
				Without.		With CaCO ₃ .		Soluble.		Vegetable test.
				Per cent.	Rank.	Per cent.	Rank.	KMnO ₄ .	Pepsin.	
Series I.										
Dried blood	34·8	100	54·9	100	94·4	94·7	73·3			
Cotton-seed meal	33·9	97	54·8	100	91·1	91·1	64·8			
Dried fish	30·3	87	46·5	85	88·7	67·3	63·9			
Tankage	26·2	75	34·8	63	88·3	56·4	49·4			
Bat guano	22·4	64	35·8	65	75·1	56·4	—			
Bone	18·9	54	16·6	30	64·2	92·3	16·7			
Bone (six weeks)	21·7	—	17·4	—	—	—	—			
Ammonium sulphate	1·3	4	31·1	55	100	100	—			
Sodium nitrate	—	—	—	—	100	100	100			
Series II.										
Cotton-seed meal	26·7	—	—	—	—	—	—			
Ammonium sulphate	3·4	—	32·6	—	—	—	—			

decreased by the addition of calcium carbonate, while that of ammonium sulphate is increased enormously. These results show the beneficial influence of lime in rendering nitrogenous fertilisers available, and explain in part why lime is so beneficial to many crops.

When ammonium sulphate is used as a fertiliser, it would be advisable to add calcium carbonate at the same time, in many cases.

Nitrification of Ammonium Sulphate.

As regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilising materials tested. In the soil to which calcium carbonate has been added, the rate of its nitrification still falls below that of cotton-seed meal, blood, and dried fish, and was in one series less, the other greater, than tankage and bat guano, but the average was below. In Bonâme's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilising materials used (blood, oil cake, guano), whether calcium carbonate was added or not. On the contrary, the experiments of Müntz and Girard (presumably in a soil containing calcium carbonate), place ammonium sulphate at the head of all the fertilising materials tested (blood, flesh meal, poudrette, roasted leather, leather chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

1. Ammonium sulphate may hinder the action of the nitrifying organism. The soil in question contained 2·5 grms. ammonium sulphate dissolved in 100 grms. of soil water. It is known that various salts will retard the nitrifying activity of the organisms if present in too large quantity. Deherain found that common salt began to be harmful when more than 0·1 per cent of the weight of the soil was added, and with larger quantities nitrification almost ceased. Large additions of sodium nitrate also decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the ammonium carbonate formed is more of a hindrance to the germs than the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained. It would also explain the results of Bonâme (already cited), according to which ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Müntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, &c., and those of Th. Schloesing (*Central-Blatt. Agr. Chem.*, 1890, xix., 1, abs.). The latter found that at the end of fifty-six days ammonium chloride added

to a soil at the rate of 3·58 grms. per kilo. (1·8 grms. per 100 c.c. of soil water), was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2·7 grms. per kilo. (1·4 grms. per 100 c.c. soil water), in twenty-two days, and ammonium carbonate at the rate of 0·53 gm. ammonia per kilo. in twenty-eight days. The soil contained 10·4 per cent water.

These difficulties might be explained by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, &c.), or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertiliser, though perhaps to a less degree. Each lump of the salt would become a centre from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavourable condition to disappear, would depend on the rate of diffusion of the salt, soil, moisture, rainfall, &c.

2. The second explanation for the slow rate of nitrification of ammonium sulphate compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being only neutralised in part by the bases of the soil. When calcium carbonate is added, it neutralises the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for if so, the addition of calcium carbonate would remove the unfavourable conditions, and place ammonium sulphate at the head of the list, which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to nitrites more readily. The nitrites are then converted to nitrates. In soils containing the first kind of organisms, and few of the second, organic matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Bonâme and those here described. In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited.

It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others. It is the purpose of this Station to continue the experiments on nitrification, with a view to test all the problems that may arise.

Conclusions.

1. The nitrification of blood takes place more rapidly

when it is mixed with a large quantity of soil than with a small quantity.

2. The order of nitrification in the soil used was, dried blood (most nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate. Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests and solubility in potassium permanganate.

3. When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became, dried blood, cotton-seed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.

4. When ammonium sulphate is used as a fertiliser, in most cases it would be advisable to add calcium carbonate in some form also.

5. The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts. The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms. The acids formed may also be a hindrance when no base is present to neutralise them. All three of these causes may be in operation at the same time.

CORRESPONDENCE.

THE DIRECT ESTIMATION OF CARBON IN METALS.

To the Editor of the Chemical News.

SIR,—I am obliged to Mr. McIntosh for his information relating to the sharp practices of the paint trade. This knowledge, however, does not appear to have especially qualified him to deal with the direct estimation of carbon in refractory alloys.

Unfortunately the worse kinds of red-lead were not preserved, and I am therefore unable to make any further examination of them in order to convince Mr. McIntosh that they were not merely "barytes dyed with a coal-tar colour." Their general behaviour during and appearance after fusion, however, favours the conclusion that they were mixtures of oxides of lead with a red colour. Moreover, one of these which gave a blank of 0.0674 on 10 grms. was in regular use in a neighbouring laboratory for the purpose of estimating manganese in steel by that process where permanganate is formed by boiling a nitro-sulphuric solution with red-lead. It can hardly be claimed that "barytes dyed with a coal-tar colour" will oxidise managanous salts to permanganate.

Even when red-lead consists substantially of lead and oxygen only it is rarely Pb_2O_4 . It has been shown in a volume of the *Journal of the American Chemical Society* (for the year 1897, I think), to which I have no means of referring, that commercial red-lead almost invariably contains an excess of PbO over and above that needed to form $2PbO.PbO_2$. I imagine that this excess of PbO might be the cause of the blank, on account of the facility with which it takes up CO_2 from the air. This explanation of the blank, which occurs even when the possibility of trade trickery is eliminated, is the most obvious one.

As though halting in his conviction that red-lead free from CO_2 was easy to obtain, Mr. McIntosh banishes it altogether, and purposes to use lead chromate prepared on the spot. If he had ever actually tried this experiment he would know, even supposing the reagent were free from blank (?), that the whole of the carbon could not be got from a rich ferrochromium say, except at temperatures very much beyond those obtainable in the average combustion furnace. Chromate of lead strongly fused and powdered is a much more effective reagent, but Mr. McIntosh would have to reject it "even if the blank were completely negative," because it certainly does not "dissolve instantaneously in a large excess of potash."

Perhaps Mr. McIntosh would find in practice, if he avoided the "know nothing and care less" kind of dealer, that more purposeful knowledge could be gained by a "blank" experiment than by the tests he mentions.

It only remains to point out that the blank referred to is the increased weight of the KHO bulb after ignition of the sample, and not the percentage of carbon calculated therefrom, as Mr. McIntosh has assumed.—I am, &c.,

HARRY BREARLEY.

Totley, near Sheffield,
July 29, 1901.

ESTIMATION OF AMMONIA IN ITS SALTS.

To the Editor of the Chemical News.

SIR,—Mr. Bennett Blackler in the *CHEMICAL NEWS* (vol. lxxxiii., p. 299) draws attention to what he calls a new method of indirectly estimating ammonia in ammoniacal salts.

It may interest him to hear that this is an old and well-known method: personally I was taught it twenty years ago by the late Dr. Dittmar in Anderson's College, Glasgow, and since then have constantly used it, more especially in the testing of sulphate of ammonia.

The following working details are much better for commercial sulphate of ammonia:—Weigh out 3 grms. of the sample, dissolve in water, in a porcelain basin, add methyl orange, neutralise with normal caustic soda, add 50 c.c. normal caustic soda solution, boil, and after cooling, titrate back with normal sulphuric acid. Each c.c. soda solution consumed corresponds to 17 m.grms. NH_3 .—I am, &c.,

ALEXANDER BUCHAN.

13, Willowbank Crescent, Glasgow,
July 22, 1901.

THE TINTOMETER IN WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—Would any reader of the *CHEMICAL NEWS* be kind enough to acquaint me with his experience, if any, of using a tintometer in connection with water analysis for the purpose of estimating ammonia by means of Nessler's solution? Or, failing this, has a tintometer ever been used for this purpose?—I am, &c.,

E. R. DEACON.

AN INSPIRATION FROM THE IMMORTALS.

To the Editor of the Chemical News.

SIR,—Ordinary mortals are indebted to *L'Illustration* for a picture representing one of the "Forty Immortals," engaged in the "meditations, calculations, and experiments" which enabled him to "solidly build up organic chemistry on the positive basis of synthesis," and kodaked in the act of permitting "conquered matter to operate in a closed vessel," provided with a thermometer so delicate that he is reading it with a magnifying glass (at an angle of about 45°), while grasping it with his fingers at a point well below the top of the mercury column.—I am, &c.,

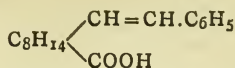
DIAZO.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

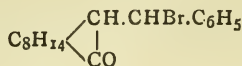
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 2, July 8, 1901.

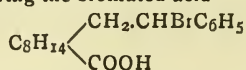
New Derivatives of Benzylcamphor and of Benzylidene-Camphor.—A. Haller and J. Minguin.—The author's researches show that the non-saturated acid—



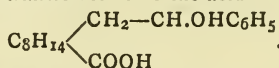
which is produced when benzylidene-camphor is treated with hot hydrobromic acid or the bromated benzyl-camphor—



by potash or alcoholic ammonia, fixes a molecule of hydrobromic acid, giving the bromated acid—

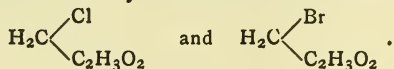


This acid when heated with an acetic solution of hydrobromic acid is transformed into the acid—



Manganic Phosphates.—V. Auger.—The author's researches were carried out chiefly on the violet solution which forms the product of fusion of manganese nitrate and phosphoric acid heated to about 210° . The molten mass, when dissolved in water and left for some days, deposits a rose-coloured crystalline crust, manifestly a mixture of two or three products. Herrmann analysed a portion of this crust and found it correspond to the formula $\text{Mn}_4\text{P}_6\text{O}_{21}\cdot 8\text{H}_2\text{O}$. The author isolates from the same mass a hydrated salt in a pure state, and finds it to have a formula differing from Herrmann's only in the amount of water of crystallisation, $\text{Mn}_4\text{P}_6\text{O}_{21}\cdot 14\text{H}_2\text{O}$. This salt is certainly a pyrophosphate, for when treated in the cold by an alkali, it gives an alkaline phosphate which possesses all the reactions of pyrophosphoric acid. Manganic metaphosphate, MnP_3O_9 , was also isolated from the crust and found to be anhydrous.

Action of Acid Chlorides on Methanal.—Louis Henry.—The author investigates the action of pentachloride and pentabromide of phosphorus on polymerised methanal, which action causes the latter to be transformed into $\text{H}_2\text{C}\cdot\text{Cl}_2$ and HCBBr_2 . He also examines the action of acetyl chloride and bromide on the same body, an action which furnishes methylene chloro- and bromo-acetates—



Action of Vegetable Alkaloids on certain Indicators.—A. Astruc.—Vegetable alkaloids act on various indicators in a different manner, varying not only according to the group to which they belong, but also with the dissociating power of the liquid in which they are dissolved. As there exists a perfectly symmetrical relation between the thermometric constants and the alkalimetric or acidimetric constants, the results of the calorimetric determinations effected in various media, which are already in course of experiment, may be predicted.

Di-naphthoxanthene.—R. Fosse.—The author prepares the mono-chloro and mono-bromo derivatives and also an amine of di-naphthoxanthene in order to compare these bodies with the hydrochloric and hydrobromic ethers and the amine of the pretended binaphthyleneglycol. He discovers in these derivatives of di-naphthoxanthene curious properties about which nothing can be found up to the present time in chemical literature and no analogous examples amongst non-nitrated bodies.

Nitration Product of Acetylacetic Ether.—L. Bouveault and A. Bongert.—M. Scholl prepared, amongst the highest products obtained by the action of silver nitrate on ethyl bromacetate, a liquid whose boiling-point is close to that of the substance the authors obtained during the nitration of acetylacetic ether. The two substances possess the same composition and the same molecular weight. The authors' first idea was to conclude the identity of

these two substances, but their present research proves them to be distinct isomers.

A Method of Synthesis of Acetylenic Aldehydes.—Ch. Moureu and R. Delange.—The authors' method of synthesising acetylenic aldehydes is by condensing the formic ethers with acetylenic carbides. Experiment shows that the formic ethers attack the sodium carbides, $\text{R}\cdot\text{C}\equiv\text{CNa}$, with energy, and that the final action of water on the crude product of reaction causes the formation of the acetylenic aldehydes, $\text{R}\cdot\text{C}\equiv\text{C}\cdot\text{CHO}$. The operation should be performed at a low temperature (about 0°).

MISCELLANEOUS.

Action of Contact on Secondary and Tertiary Alcohols.—A. Trillat.—The author's experiments show that the action of a platinum spiral is manifested not only on primary alcohols, but also on secondary and tertiary alcohols, with formation either of ketones alone or of ketones and formaldehyde. In all these cases the heat given out by the chemical reaction is sufficient to maintain the platinum spiral in a state of incandescence.—*Comptes Rendus*, cxxii., No. 24.

Action of Sulphuretted Hydrogen on Acetylacetone.—F. Leteur.—If acetylacetone or its aqueous solution is submitted to a current of sulphuretted hydrogen, no perceptible action takes place; this gas does not act well on the solution in acetic acid solution, even in presence of fused sodium acetate, but if a solution of 20 grms. of acetylacetone in 100 c.c. of strong hydrochloric acid is submitted to the same treatment, at the end of some hours needle-shaped flakes are deposited. At the end of about twenty hours the action apparently terminates, and an abundant crystalline deposit is obtained, which on examination is found to have the formula $(\text{C}_5\text{H}_8\text{S}_2)_2$, and is a dimer of the pentanedithione-2.4.—*Comptes Rendus*, cxxxiii., No. 1.

UNIVERSITY OF BIRMINGHAM.

FACULTIES OF SCIENCE AND ARTS.

1901-2.

The SESSION will commence on TUESDAY, OCTOBER 1st, 1901.

The UNIVERSITY confers DEGREES in SCIENCE (including ENGINEERING) and in ARTS upon Students who have attended prescribed University Courses of Study. These Courses are also open to all who may wish to join them, whether Candidates for Degrees or not.

EXHIBITIONS, SCHOLARSHIPS, PRIZES, &c., are offered for competition.

DIPLOMAS in EDUCATION are granted to Candidates fulfilling the required conditions.

SPECIAL TECHNICAL COURSES are provided in Engineering (Civil, Mechanical, and Electrical), Metallurgy, Applied Geology, and in Malting and Brewing.

For the present, the University also provides PRELIMINARY COURSES in preparation for the MATRICULATION EXAMINATION of the University, and for other purposes.

SYLLABUSES of the Faculties of Science and Arts, and of the School of Malting and Brewing, are now ready, and may be obtained gratis from Messrs. CORNISH, New Street, Birmingham, or on application at the University.

There is also a Faculty of Medicine (including a Department of Dentistry). A Syllabus containing full particulars is published separately.

THE

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided

for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 30th; Lectures begin October 8th, 1901.

Hostels for Men and for Women Students.

Prospectuses on application to the SECRETARY.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2176

ON THE MIXED ESTERS OF CELLULOSE, AND THE RELATIONSHIP OF CELLULOSE TO NITRATING ACIDS ($\text{HNO}_3\text{--H}_2\text{SO}_4$).*

By C. F. CROSS, E. J. BEVAN, and R. L. JENKS.

We have recently investigated a number of mixed esters of the celluloses and lignocelluloses, more especially the aceto-benzoates and nitrobenzoylnitrates, the results of our investigations having been published elsewhere (Cross and Bevan, "Researches on Cellulose, 1895-1900," Longmans, London, 1901). These mixed esters have been produced for the most part by the successive action of the respective esterifying reagents, the most convenient procedure being to fix first the benzoyl groups upon the cellulose, and to treat the resulting benzoates with acetic anhydride, or for preparing the mixed nitrates, with the usual nitrating mixtures. From the study of the quantitative relationships of these derivatives we have been able to throw some further light on the functions of the OH groups of the celluloses, and from a closer investigation of the reactions we are able to conclude that cellulose in the presence of a mixture of negative radicals under esterifying conditions will combine simultaneously with two or more according to the usual laws governing such reactions.

Without entering into a full discussion of this complicated problem, which we reserve until our investigations are more complete, we wish to deal with the specific case of the formation of the nitric esters by the usual method of treating the fibrous celluloses with a mixture of nitric and sulphuric acids. The function of the latter acid has invariably been assumed to be the indirect one of combining with the water liberated in the reaction between cellulose and the nitric acid; and this general conclusion from the literature of the subject is expressly adopted in the latest investigations of the reaction (Lunge and Bebie, "Beitrag zur Kenntniss der Nitrocellulose," *Ztschr. Angew. Chem.*, 1901, Heft 20).

From our investigations we were led to the conclusion that it was *a priori* improbable that sulphuric acid should play this inert rôle in relation to the cellulose, and we have now positive proof that it takes a direct part in the reaction. There are two ways in which the function of combining directly with the cellulose OH-groups may be exerted:—(1). A cellulose sulphuric ester may be formed and immediately decomposed, the NO_3 residue taking the place of the SO_4H residue at first fixed. In this case no evidence of such action would be furnished by the properties or composition of the product. (2). There may be produced as the first product of the joint action of the acids a mixed nitric-sulphuric ester of sufficient stability to persist in the acid mixture, and to withstand the subsequent action of water. In this case the fixation of sulphuric residues will be proved by a simple analysis of the products.

It is this second and more important case which we are able to establish by the following experimental proof. A complete diagnosis of the former will require more extended investigation. Positive evidence, however, is to hand as to the influence of H_2SO_4 in relatively minute proportion.

Samples of selected American cotton were nitrated with a mixture of acids in the usual proportion $\frac{\text{HNO}_3}{\text{H}_2\text{SO}_4} = 1/3$ by weight, the proportion of water alone being varied.

A Paper communicated to the *Ber. Deuts. Chem. Ges.*, July 4, 1901.

Series 1. The action was continued for one hour at 16°C , the products then washed and exhaustively purified by treatment with boiling water until the wash waters were entirely free from acid products. This required ten to fifteen hours' boiling, the wash water being changed every forty-five minutes. The nitrates were dried and weighed to determine yield, and afterwards destructively oxidised for the estimation of H_2SO_4 .

H_2O per cent.	Nitrating acid, $\text{H}_2\text{SO}_4/\text{HNO}_3$.	Yield.	Per cent H_2SO_4 combined with cellulose in product.
10.14	3/1	171.3	0.00
2.3	3/1	170.6	0.23
0.0	3/1	122.25	a 0.83
			b 1.00
0.0	3/1	135.0	1.35

These numbers establish the fixation of the sulphuric residue in combination with the cellulose, the quantity increasing as the acid mixture approaches to the condition of pure "monohydrate."

On the basis of incidental observations we now aimed at an increased fixation of sulphuric acid in the products by reducing the duration of exposure to the acid mixture from sixty to seven minutes. The conditions of purification of the products were also changed, the nitrates being exhaustively washed with cold distilled water, each successive quantity of water being titrated to determine the rate of elimination of the acids. When wash water and nitrate were neutral in reaction the latter was dried off to determine yield, and then destructively oxidised for the determination of H_2SO_4 .

Two series of experiments were made—(a) with bleached cotton, (b) with unbleached. In order to refer the numbers for H_2SO_4 to a uniform basis they are calculated to the weight of the original cotton taken for nitration.

H ₂ O per cent.	Nitrating acid, H ₂ SO ₄ /HNO ₃ .	Yield of nitrate.	H ₂ SO ₄ fixed.	
			Per cent of product.	Per cent of original cellulose.
(a) <i>Bleached Cotton.</i>				
10.13	3/1	152.7	2.56	3.91
2.30	3/1	162.2	2.52	4.06
0.0	3/1	134.4	4.62	6.21
(b) <i>Unbleached Cotton.</i>				
10.13	3/1	171.55	2.59	4.17
2.3	3/1	163.3	1.87	2.86
0.0	3/1	132.6	1.52	1.89

It is evident that the H_2SO_4 combined is easily eliminated from the nitrates prepared under the ordinary conditions with a somewhat diluted acid mixture, *i.e.*, the sulphuric ester groups are hydrolysed by the ordinary purification process of boiling with water, &c. We also find that the ester groups in question are eliminated by treatment with diluted acetone containing sufficient water to prevent the ordinary solvent action of the acetone upon the nitric esters (Luck and Cross, *Journ. Soc. Chem. Ind.*, 1900, 642). By this treatment we hope to effect a separation of the particular mixed esters in question.

As previously noted, this investigation of the nitrates is only a special case in a systematic enquiry into the relationship of the celluloses to the several negative radicals with which it was previously known to form well-defined compounds, *viz.*, the nitrates, benzoates, acetates, and sulphates.

We make a separate preliminary communication on this case in view of the special interest attaching to the nitrates, and as a direct contribution to the practical question of the causes of instability of the nitrates.

We have pleasure in acknowledging the co-operation of our friend Dr. R. Messel in this scheme of research.

ADDENDUM, July 31, 1901.—Since the date of writing the above preliminary communication the experimental evidence has accumulated. The empirical fact of the fixation of sulphuric acid in combination with the cellulose

lose had been carefully separated from all possible errors of analysis, or of conditions of purification of the products. The later investigations have been extended to the conditions of breaking down—by hydrolysis—and of fractionation of the products by graduated solvent actions, with a view to eliminate the mixed ester product assumed to be formed, in the first case, in the form of products of decomposition, and, in the second, as an undecomposed cellulose derivative. It is in these directions that the evidence continues to accumulate that a mixed cellulose nitro-sulphuric ester is formed under certain regulated conditions of treatment with the mixed acids, and that in all cases where cellulose is in presence of both nitric and sulphuric acids, a positive combining function of the latter has to be reckoned with.

4, New Court, W.C., and
89, Bartholomew Close, London, E.C.,
July 1, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc. R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

THE advances which have been made in recent years in the metallurgical processes for the successful treatment of complex auriferous ores have led to the adoption of special methods of assay for this class of material.

In this paper the author deals with the principal methods which are used for estimating the precious metals in complex ores.

The expression, "complex ores," includes those ores in which the gold is associated with gangues of basic oxides, such as ferric oxide, alumina, lime, &c., and with metallic sulphides and sulph-arsenides, such as iron and copper pyrites, arsenical iron pyrites, sulphides of antimony and of bismuth, zinc blende, and galena. Those ores are also included in which the gold exists in chemical combination with another substance, as with tellurium in the minerals graphic tellurium (sylvanite), calaverite, and foliated or black tellurium (nagyagite), a class of ores which has attracted considerable attention within recent years.

Many text-books on assaying give universal mixtures for the assay of all classes of complex auriferous ores, but it is obvious that, if reliable results are to be obtained, complex ores must be assayed on scientific principles, each ore being treated with the fluxes and reagents best suited to its composition.

As the selection of the fluxes and the quantity of each to be employed is dependent upon the richness of the ore, the nature of its gangue, and the presence or absence of compounds of the base metals, it is impossible to give definite charges to meet the requirements of all classes of ore; the best method to be used in each particular case must therefore necessarily be left to the judgment and experience of the assayer. The chief fluxes used in the assay of gold ores are sodium carbonate, which is a flux for silica and silicates, and borax, which acts as a flux for lime, oxide of iron, and other bases. The relative quantity of each of these fluxes must be varied according to the nature of the material to be assayed; a mixture of equal weights usually answers very well. One and a half parts of sodium carbonate are required to satisfactorily flux one part of silica.

Powdered sand or glass may be used with advantage as a partial or complete substitute for borax, especially with materials rich in metallic oxides.

Litharge is a powerful base, and is sometimes used to flux siliceous materials. It is a very useful flux under certain conditions, as it forms fusible compounds with oxides that are infusible alone, and on this account there

is sometimes an advantage in having an excess of lead oxide in the slag. This is particularly the case when oxides of copper are present in the material to be assayed. Red-lead is frequently used instead of litharge.

Lead oxides are used chiefly as a source for lead for collecting the gold and silver, but they are occasionally employed as oxidising agents to oxidise sulphur, arsenic, antimony, &c. Red-lead is used with advantage for pyritic gold ores where an oxidising action is required in the fusion, while litharge, which contains less oxygen, is well adapted for ores with much quartz, or where the conditions of the fusion are reducing.

Carbon, chiefly as charcoal, is largely employed as a reducing agent. Flour or argol may be substituted for charcoal where the latter is not to be conveniently obtained. Two grms. of flour or 5 grms. of argol equal 1 grm. of charcoal in reducing power.

Nitre is a powerful oxidising agent, and is used with advantage to oxidise compounds of the base metals present in certain complex ores which cannot be conveniently oxidised with hot air. For materials containing sulphates of baryta or lime, or phosphate of lime, fluor-sparg may be added with advantage, as it helps to increase the fluidity of the charge.

The amount of flux required is judged in the first place from the appearance of the ore, and is subsequently modified according to the result of the fusion. It is well in this connection to bear in mind the general principle that for basic material an acid flux is needed, and for an acid or siliceous gangue a basic flux. Three parts of flux are usually quite sufficient to yield a fluid slag with one part of ore, but if it be found that this is not sufficient the remedy lies in using a different flux rather than in taking a larger quantity.

All samples of complex ores should be reduced to fine powder and passed through a sieve of 80 holes to the linear inch. The question of fine powdering is of much importance in dealing with complex ores.

The assay of gold ores is in most cases conducted by the fusion or crucible process, but occasionally the scorification process is used.

Wet methods are scarcely applicable owing to the extremely small proportion which the gold bears to the worthless gangue with which it is accompanied. In exceptional cases a combined wet and dry process may be employed with advantage.

The crucible methods of assaying complex ores vary somewhat according to the nature of the substances to be operated upon, and will for convenience be described under the following heads:—

Basic oxidised ores.
Pyritic ores.
Telluride ores.
Bismuth ores

Basic Oxidised Ores.

The chief ores which come under this head are those consisting mainly of limonite or hydrated oxide of iron. Ores containing magnetite, calcite, and dolomite, and those which are largely composed of the sub-crystalline, slaty, or schistose rocks, may also be included under this head.

One of the chief considerations in the assay of materials consisting chiefly of ferric oxide (Fe_2O_3) is the reduction of the higher oxide to the ferrous state (FeO), in which state alone it unites with silica to form a readily fusible compound. Ferric oxide being infusible, its presence in the slag tends to stiffen it and render it pasty. Experience has shown that the separation of the gold in the ore is more or less incomplete when much ferric oxide is present in the slag. The reduction of the iron to the state of the lower oxide is effected by the addition of charcoal powder or other reducing agent to the charge, the quantity added being in excess of that needed to provide the lead for collecting the gold. With ores consisting mainly of ferric oxide the quantity of charcoal powder required will be

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

about one-twelfth part of the weight of ore taken for assay; the exact amount needed for any particular ore must, however, be left to the experience of the assayer.

The proportion of alkaline flux required for ores containing much iron oxide is comparatively small, as the ferrous oxide formed during the fusion combines with silica, with the production of ferrous silicate, which is easily fusible. The addition of alkaline fluxes results in the formation of double silicates, which greatly increase the fusibility of the slag. It may be pointed out, however, that the addition of proportionately large quantities of alkaline flux to ores containing oxides (such as iron and manganese), which form easily fusible silicates, is a decided disadvantage, inasmuch as they cause the charge to melt too rapidly, and thus prevent the complete collection of the precious metals. As a general rule the proportion of sodium carbonate should be diminished as the quantity of metallic oxides in the ore becomes greater, while the proportion of borax, lead oxide, and charcoal should be increased.

Sodium carbonate may be altogether omitted for ores practically free from siliceous material, and the deficiency of silica allowed for by the addition of fine sand or powdered glass, otherwise excessive corrosion of the crucible will result.

For ores ranging from moderately basic (with about 30 per cent of ferric oxide), to very basic, the following proportions may be taken:—

	Moderately basic. Grms.	Very basic. Grms.
Ore	50	50
Litharge	40	50
Charcoal powder	2.5	4 to 6
Borax	20	30
Sodium carbonate	30	10 to 15
Sand or glass	Nil	10 to 20

The charge should be covered with a layer of powdered salt to prevent the oxidation of the slag.

The lead button resulting from the fusion should weigh from 25 to 35 grms., and with ores practically free from iron oxide 2 grms. of charcoal are sufficient to produce this result; but as the proportion of iron oxide increases, the amount of carbon must also be increased for the reason stated above. For ores consisting mainly of iron oxide, 4 grms. of charcoal are usually sufficient to produce the desired weight of lead, but in exceptional cases a larger quantity may be required. A sample of gold ore, practically pure hæmatite, assayed by the author, required 6 grms. of charcoal; another sample which was mainly micaceous hæmatite also required this amount. In both cases 20 grms. of fine sand were used, the quantities of the other fluxes being the same as those given above. If more than the desired weight of lead is obtained, it should be reduced to convenient size by scorification, since less loss of the precious metals is incurred by scorifying lead than by cupelling it.

Peroxide of manganese is not commonly associated with gold ores, and if present it is usually in small proportion only. It requires about twice the amount of charcoal for its reduction to the lower oxide as compared with iron oxide; due allowance must therefore be made in the amount of charcoal added when large proportions of peroxide of manganese are present. The quantity of litharge should be slightly increased for ores containing small quantities of copper or antimony oxides, the amount required being usually from 60 to 70 grms. for a charge of 50 grms. of ore. The excess of lead oxide passes into the slag, and carries the copper and antimony with it, thus preventing the production of cupriferosus or antimonial lead.

For ores consisting mainly of earthy bases—such as lime, alumina, &c., or of zinc oxide—the quantity of alkaline flux is advantageously increased to 60 grms. A piece of hoop iron should be added to the charge for ores containing small quantities of iron pyrites, for the reasons stated in the section dealing with pyritic ores.

The fusion of the charge is an operation which too frequently receives but scant attention at the hands of the assayer, but it may be pointed out that the success or failure in collecting all the gold in the sample is to a large extent dependent on the care bestowed on the fusion. This remark is specially applicable to ores containing much ferric oxide. The crucible is placed in the furnace at a red heat, and the temperature gradually raised to full redness. The temperature should not be raised too rapidly at first; a dull red heat is maintained for about ten minutes to ensure the complete fritting of the charge before actual fusion takes place; this is a point which is frequently neglected. Rapid increase of temperature will cause a quick evolution of carbonic acid from the decomposition of the alkaline carbonate, and a corresponding loss from projection. When effervescence has ceased, and the contents of the crucible have become thoroughly liquid and tranquil, it is removed from the furnace, and its contents poured into an ingot mould. The time which elapses from the introduction of the charged crucible into the furnace to the final pouring usually varies from thirty to forty minutes. Prolonged or excessive heating should be avoided, as it tends to thicken the slags. The button of lead should weigh from 25 to 35 grms., and the amount of charcoal added to the charge must be altered as may be necessary to secure this end. The lead is cupelled, and the resulting gold-silver button weighed and parted in dilute nitric acid in the usual way.

It is not usually necessary to clean the slags from the assay of gold ores, but when the ores are very rich and contain large quantities of the oxides of iron or of manganese it is very advisable to do so. For this purpose the slag is collected, roughly powdered, and "cleaned" by mixing with the following charge:—

Litharge	30 grms.
Charcoal powder	1.5 "
Sodium carbonate	10 "

The charge is placed in the crucible previously used for the fusion and kept in a molten state from ten to fifteen minutes. If the fused product is thick and pasty, a small quantity of borax may be added with advantage. The button of lead obtained in this fusion is either cupelled by itself or with the assay button previously obtained.

Pyritic Ores.

Native gold, *in situ*, is most frequently met with in quartz veins intersecting metamorphic rocks, and is almost invariably associated with iron pyrites and other metallic sulphides and sulph-arsenides, which are also technically known as "sulphurets."

Under these conditions it is not surprising that the larger proportion of complex ores with which the assayer has to deal comes under the somewhat vague title of "pyritic ores." In order to facilitate the description of the various processes adopted for the assay of ores of this class, the following subdivision will be made:—

- Pyritic ores (mainly iron pyrites).
- Arsenical ores.
- Antimonial ores.
- Cupriferosus ores.
- Ores with galena and zinc blende.

The author is well aware that in pyritic ores it is more usual to find several sulphides associated with the ore than to find one sulphide only, and due consideration will be given to this fact in dealing with the different sulphides enumerated.

Pyritic Ores (mainly Iron Pyrites).—The assay processes for the treatment of pyritic ores are chiefly based on the various methods employed for the removal of the sulphur.

The elimination of the sulphur is necessary, otherwise it will pass into the lead, making it more or less brittle, or the lead will be accompanied by a layer of regulus or artificial sulphide.

The methods for the removal of the sulphur may be summarised as follows:—

- (a) Oxidation by roasting.
- (b) " with nitre.
- (c) " with lead oxide.
- (d) Desulphurisation with metallic iron.

Method (a).—The elimination of the sulphur by an oxidising roasting of the ore previous to fusion is undoubtedly the most satisfactory method of dealing with pyritic ores in which iron pyrites or mispickel predominates.

Many assayers, however, hesitate to roast their ores, on the assumption that gold is lost during the process. Although this may be true when proper precautions are not taken, it may be remarked that the loss of gold experienced is, in many cases, more probably due to want of care in conducting the operation, or to the retention of gold in the slag owing to improper adjustment of the charcoal in the charge for fusing the roasted ore.

The quantity of ore to be used for assay should be weighed out before roasting. The roasting is most conveniently effected in shallow clay dishes in a muffle or in the crucible in which the fusion is subsequently performed. The temperature at which the roasting is started is not a matter of indifference, as it is during the first few minutes of the operation that the formation of lumps is most to be feared. A dull red heat should be employed at first, and the ore frequently stirred, though not violently, to expose fresh surfaces to the air, and to prevent fritting. The employment of too high a temperature at the outset, or neglect in stirring, will cause partial fusion of the sulphides, and the formation of matter troublesome to roast. The ore is maintained at dull redness until all blue flame has ceased and no incandescent particles are visible on stirring, after which the temperature is raised to full redness to decompose sulphates.

A high temperature at the outset facilitates the formation of arseniates and antimonates, and will frequently cause a mechanical loss of gold and silver owing to the rapid disengagement of the volatile constituents of the ore, the vapours of which tend to carry off the precious metals. The mechanical loss during roasting may be considerable when proper precautions are not taken. The chief causes of loss are excessive agitation of the ore and decrepitation of the pyritic material, due in many cases to the coarseness of the powdered sample.

The roasting, which occupies from thirty to sixty minutes for 50 grms. of ore, is complete when the ore remains of a uniform colour on stirring, and no more fumes of sulphurous acid can be perceived. Excessive or prolonged heating of the ore should be avoided, as it tends to produce magnetic oxide ($3\text{Fe}_2\text{O}_3 = 2\text{Fe}_3\text{O}_4 + \text{O}$), which is undesirable, since this oxide is more difficult to flux than ferric oxide.

Arsenates and antimonates are stable at high temperatures, and will cause loss of precious metals in the subsequent fusion of the roasted material unless previously decomposed. The reduction of these compounds and also of sulphates is effected by mixing a small quantity of charcoal or anthracite powder with the ore after it has been completely oxidised, and roasting again for a short time at a bright red heat. Arseniate of iron is readily decomposed when heated with charcoal powder, and practically the whole of the arsenic eliminated, but the reducing action of charcoal on arseniate of copper is very small, only a slight elimination of arsenic taking place. Hence it is very necessary in the case of arsenical ores, especially when copper is present, to effect the elimination of the arsenic as completely as possible during the early stage of the roasting. Antimonates are also decomposed by charcoal, but less easily than most arseniates, the antimony being eliminated to a large extent on re-roasting.

Ores containing tellurium or large quantities of antimony or of lead should not be roasted, ores of this description being more satisfactorily treated by special methods.

The fusion of the roasted ore is effected in the same manner as described for ores with much metallic oxides, to which class they belong.

Experience will frequently enable the adjustment of the charcoal to be made from the colour of the roasted ore.

(To be continued).

A NEW INDICATOR FOR USE IN DETERMINING TOTAL ACIDITY OF WINES.*

By E. G. RUNYAN.

In maintaining a chemical control of a beet-sugar house, it is often necessary to determine by some rapid method the excess of alkali in the juices, syrups, and massecuites. The usual method is to titrate the material with a standard acid solution. As these products vary in colour from a light amber to a dark brown, or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, in 1892, proposed a mixture of corallin and malachite green prepared as follows:—

Three and one-tenth grms. of corallin or commercial rosolic acid are dissolved in 150 c.c. of 90 per cent alcohol, neutralised and mixed with 0.5 gm. malachite green dissolved in 50 c.c. of alcohol. With this mixture alkalis give a purple colour, which is changed to a green by acids.

Malachite green dissolves in alcohol, yielding a greenish blue solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colours of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly coloured sample of beet molasses, and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly coloured products as wines, vinegars, and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly coloured wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows:—

"Transfer 10 c.c. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red colour changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus-paper shows an alkaline reaction."

Another method in use by some chemists is to dilute 10 c.c. of the wine to about 300 c.c. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution, and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured—(1) a claret, as a type of red wine; (2) a Rhine wine for the white type; and (3) a sherry for the

* Read before the Washington Section of the American Chemical Society, March 14, 1901. From the *Journal of the American Chemical Society*, xxiii., No. 6.

† The zinc-double-chloride of tetramethyldi-*p*-amidotriphenyl-carbinol, $(\text{C}_{25}\text{H}_{22}\text{N}_2\text{Cl}_2)_2 + 2\text{ZnCl}_2 + 2\text{H}_2\text{O}$.

medium colour. In this experiment the following method was employed:—

Transfer 10 c.c. of the sample to a beaker, dilute with about 300 c.c. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of decinormal sodium hydroxide solution, indicated by a purple colour, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green colour. The change in colour is best observed by transmitted light. A trial showed that that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator was used, and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 c.c. decinormal sodium hydroxide solution = 0.0075 grm. tartaric acid. The following are the results obtained:—

Grms. Tartaric Acid in 100 c.c. of Wine.

Wine.	Corallin-Malachite.	Phenolphthalein.	Litmus.
1. Claret.. ..	0.840 0.870 0.870 0.880 0.875	0.995 0.980 0.980 — —	0.890 0.920 — — —
Average ..	0.867	0.985	0.905
2. Rhine Wine..	0.705 0.710 0.705 6.695 0.705 0.705 0.695	0.730 0.725 0.730 0.735 — — —	0.730 0.720 0.725 — — — —
Average ..	0.703	0.730	0.725
3. Sherry ..	0.450 0.430 0.440 0.445 0.435 0.430	0.490 0.475 0.475 0.475 — —	0.475 0.460 0.460 0.460 — —
Average ..	0.438	0.479	0.464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this was to be expected when we consider that with the corallin-malachite the titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret or red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of colour could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, five drops of the mixture were added to 100 c.c. of distilled water, when 0.1 c.c. of 0.1 normal hydrochloric acid solution or 0.1 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other colouring matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

ON THE METEORIC STONES WHICH FELL
NEAR ZOMBA, BRITISH CENTRAL AFRICA,
ON JANUARY 25TH, 1899.
WITH NOTES ON THE CHEMICAL ANALYSIS
OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 45).

SECTION II.—CALCULATIONS.

Interpretation of the Analytical Results.

Atomic Weights.

21. THE atomic weights used in the following calculations are those recommended by Professor F. W. Clarke, in the "Seventh Annual Report of the Committee on Atomic Weights (*Journ. Amer. Chem. Soc.*, 1900, xxii., 70; *CHEM. NEWS*, lxxxi., 146), namely:—

Al	26.9	Mg	24.1
Ba	136.4	Mn	54.6
Ca	39.8	Na	22.88
Cl	35.18	Ni	58.25
Co	58.55	O	15.88
Cr	51.7	P	30.75
Cu	63.1	Pt	193.4
Fe	55.6	S	31.83
H	1	Si	28.2
K	38.82		

It is convenient to make the calculations in the following order.

Undecomposed Material.

22. *Alkalis*.— K_2PtCl_6 0.0079 (§ 16) corresponds to KCl 0.0024; 0.0025, adherent to the filter and ignited, if taken as $Pt.2KCl$, corresponds to KCl 0.0019; making altogether KCl 0.0035. From the blank experiment (§ 8), K_2PtCl_6 0.0056 and $Pt.2KCl$ 0.0012 correspond respectively to KCl 0.0017 and KCl 0.0005; making in all 0.0022; as the direct weight of the chlorides was only 0.0021, the whole 0.0021 must have been potassium chloride. The potassium chloride due to the silicate is thus 0.0014. The mixed chlorides due to the silicate weigh 0.0183 (§ 16)—0.0021 (§ 8) or 0.0162; hence the $NaCl$ due to the silicate is 0.0148.

These amounts of $NaCl$ and KCl correspond respectively to Na_2O 0.0079 and K_2O 0.0009 for 0.4994 of undecomposed material, and to Na_2O 1.58, K_2O 0.18 per cent; no stress can be laid on the number for K_2O .

As the undecomposed material had been boiled three times, each time for five minutes, in a strong sodic solution, it is not inconceivable that soda might have been introduced into its composition. But the residue had been subjected to a very long continued washing to secure the complete removal of soluble matter; further, there is already a certain amount of sodium in the mixed silicates before the digestion with sodic solution (§ 5, § 8), and a consideration of the weights of the soda in the mixed silicates and the undecomposed material suggests that the sodium is an original constituent of the latter.

23. 0.1201 (§ 15) of mixed oxides consists of Cr_2O_3 0.0054, Al_2O_3 0.0333, Fe_2O_3 0.0808, and SiO_2 0.0006; hence 0.1545 of mixed oxides consists of Cr_2O_3 0.0070, Al_2O_3 0.0428, Fe_2O_3 0.1039 (and SiO_2 0.0008, due to the action on the glass).

Cr_2O_3 0.0070 must have been originally present as chromite ($FeO.Cr_2O_3$) and requires FeO 0.0033; chromite 0.0103 has thus been decomposed; further, undecomposed chromite 0.0027 was admixed with the main silicate. The total chromite was therefore 0.0130.

Fe_2O_3 0.1039 corresponds to FeO 0.0935; of this, 0.0033 is due to chromite, leaving 0.0902 for the silicate.

MnS 0.0042 corresponds to MnO 0.0034.

Deducting 0.0054 (§ 20) from the weight obtained for the $Mg_2P_2O_7$ 0.5384, the pure $Mg_2P_2O_7$ is 0.5330, corresponding to MgO 0.1930.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

For 0.8981 of undecomposed material (§ 15), Na_2O is 0.0141 and K_2O 0.0016 (§ 22).

Hence we have the following numbers. —

	Zomba.		Linn County.
	Percentages for silicate.	Oxygen.	Percentages for silicate.
Chromite .	0.0130	—	—
SiO_2 ..	0.5029	56.83	30.10
FeO ..	0.0902	10.19	2.26
MnO ..	0.0034	0.39	0.09
MgO ..	0.1930	21.81	8.68
CaO ..	0.0369	4.17	1.19
Al_2O_3 ..	0.0428	4.84	2.27
K_2O ..	0.0016	0.18	0.03
Na_2O ..	0.0141	1.59	0.41
Total ..	0.8979	100.00	100.00
Wt. taken.	0.8981		

The percentage composition of the silicate approaches very closely to the corresponding silicate in the Linn County meteorite as analysed by Rammelsberg (*Monatsb. Ak. Wiss. Berlin*, 1870, p. 458).

24. The undecomposed material being insoluble in water, the alkalis must be present as constituents of an insoluble compound, presumably felspar; the presence of the latter is further suggested by the fact that the dyad constituents are insufficient to form an aluminous pyroxene with the alumina and silica.

The CaO cannot be wholly present as a constituent of lime-felspar ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); for in such case the oxygen of the Al_2O_3 must have been 3.57 instead of 2.27, without the alumina required for the soda-felspar being taken into account.

Hence it is reasonable to assume:—

1. That all the alumina is due to felspar (an admixture of albite and anorthite).
2. That all the alkali is due to felspar (albite).
3. That the excess of lime above that required to form felspar is a constituent of the remaining silicate (enstatite).

With these assumptions the following numbers may be obtained:—

The oxygen of $(\text{Na},\text{K})_2\text{O}$ being 0.44, that of the Al_2O_3 and SiO_2 forming albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) will be respectively 1.32 and 5.28. The total oxygen of the Al_2O_3 being 2.27, there is left 0.95 for the oxygen of the Al_2O_3 forming anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); the oxygen of the corresponding CaO and SiO_2 will thus be respectively 0.32 and 1.28.

We therefore have the following distribution of the oxygen:—

	Total oxygen.	Oxygen of—		
		Enstatite.	Albite.	Anorthite.
SiO_2 ..	30.10	23.54	5.28	1.28
FeO ..	2.26	2.26	—	—
MnO ..	0.09	0.09	—	—
MgO ..	8.68	8.68	—	—
CaO ..	1.19	0.87	—	0.32
Al_2O_3 ..	2.27	—	1.32	0.95
K_2O ..	0.44	—	0.44	—
Na_2O ..				

The total oxygen of the bases of the enstatite, namely, 11.9, is slightly more than half that of the silica (23.54). On the other hand, the original constituents of the meteorite have been digested first with hydrochloric acid and then with sodic solution; the latter, while removing the free silica, would be expected to act to some extent on the silicates which resisted the acid, and to carry away the resultant silica, alumina, and lime, leaving the corresponding oxides of iron and magnesia from the decomposed enstatite as part of the final residue.

25. The above distribution of oxygen corresponds to the following composition for the silicates themselves:—

	Enstatite.	Felspar.		Total.
		Albite.	Anorthite.	
SiO_2 ..	44.44	9.97	2.42	56.83
FeO ..	10.19	—	—	10.19
MnO ..	0.39	—	—	0.39
MgO ..	21.81	—	—	21.81
CaO ..	3.04	—	1.13	4.17
Al_2O_3 ..	—	2.78	2.06	4.84
K_2O ..	—	0.18	—	0.18
Na_2O ..	—	1.59	—	1.59
		14.52	5.61	
	79.87	20.13		100.00

26. The composition of the above felspar is—

	Percentages.	Calculated for oligoclase (Ab_2An_1).
SiO_2 ..	12.39	61.55
CaO ..	1.13	5.61
Al_2O_3 ..	4.84	24.04
K_2O ..	0.18	0.90
Na_2O ..	1.59	7.90
	20.13	100.00

27. The percentage composition of the above enstatite is—

	Zomba enstatite.	Lodran enstatite.
SiO_2 ..	55.64	55.35
FeO ..	12.76	12.13
MnO ..	0.49	—
MgO ..	27.31	32.85
CaO ..	3.80	0.58
Al_2O_3 ..	—	0.60
	100.00	101.51

The numbers thus obtained for the Zomba enstatite are very similar to those obtained by Professor Tschermak for the Lodran enstatite; in the latter case the enstatite grains were so coarse that they could be picked out, and a sufficient amount be separated for a special analysis (*Sitzungsb. Ak. Wien*, 1870, Band lxi., Abtheil. 2, p. 465).

28. The mineral composition of the undecomposed material is—

Enstatite ..	79.87	78.71
Oligoclase ..	20.13	19.84
Chromite ..	1.47	1.45
	101.47	100.00

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 56).

B. Influence of Sulphuric Acid upon the Process of Nitration.

As already remarked, nothing above decanitrocellulose can be obtained with nitric acid alone. A higher degree of nitration can only be reached by adding a substance with an affinity for water, and of such sulphuric acid is the simplest to use. Hence, while the latter is essential to the production of gun-cotton, nitric acid alone is sufficient for collodion cotton. Yet, industrially, the lower stages of nitration are also always produced with a mixture of the two acids, on economical grounds, for in this manner there is a saving in nitric acid as well as an increase in the speed of reaction. The proportion of nitric acid to

sulphuric varies very much; in the prescriptions printed in books it varies from 1:1 to 1:6. The results obtained with the proportion 1:1 are in the tables given hitherto, especially No. III. In the following research the proportion was varied and nitration conducted at different degrees of dilution.

In order to be able to state the results directly as the action of the sulphuric acid, the ratio of the cellulose to the nitration mixture was so chosen that the ratio of the nitric acid contained in the latter to the cellulose was the same as in the first series of researches. The difference in the results must then be regarded as the action of the sulphuric acid. There were about 30 parts of nitric acid to 1 of cellulose.

The results obtained with mixtures of nitric and sulphuric acid in the ratio 1:3 are shown in the following table:—

Expt.	C.c. NO per 1 grm.	Per- centage N.	Solubility in ether- alcohol.	Increase.	Ratio cellulose: HNO ₃ .
1.	210·69	13·21	13·20	174	1:30
2.	198·10	12·42	98·70	160	
3.	186·90	11·72	99·28	157	
4.	174·81	10·96	99·50	148	
5.	187·30	11·74	99·08	159	1:12
6.	173·83	10·90	99·20	149	

The nitration mixtures had the following composition after the analyses:—

Expt.	1.	2.	3.	4.	5.	6.
H ₂ SO ₄ ..	62·18	61·53	60·30	58·88	59·77	58·34
HNO ₃ ..	21·91	20·02	19·71	19·60	20·94	20·62
H ₂ O ..	15·91	18·45	19·99	21·52	19·29	21·04

The product obtained in Expt. 2 corresponded to the pyrocollodion of Mendeleeff in nitrogen content and in solubility.

By comparing the results with Table III., we see (by means of a curve) that the rise in the ratio of nitric acid to sulphuric from 1:1 to 1:3 gives an increase in nitrogen of about 10 c.c. NO. Therefore, with the same amount of water, the ratio 1:3 attains to almost a whole stage higher than the ratio 1:1, keeping the ratio of cellulose to nitric acid constant. A decrease of the latter from 1:30 to 1:12 causes a decrease in nitrogen of about 5 c.c. NO.

A few more experiments were carried out with the ratios of nitric to sulphuric acid 1:4 and 1:5 respectively, the following being the results obtained:—

Expt.	C.c. NO per 1 grm.	Per- centage N.	Increase.	Ratio of HNO ₃ to H ₂ SO ₄ .	Ratio of cellulose to HNO ₃ .
1.	192·65	12·08	163	1:3·8	1:30
2.	179·10	11·23	153		
3.	187·58	11·76	156		1:12
4.	175·23	10·99	151		
5.	198·32	12·43	167	1:5	1:30
6.	185·89	11·66	158		
7.	168·00	10·53	140		1:8
8.	149·12	9·35	—		

Composition of the Nitration Mixtures used.

Expt.	1 and 3.	2 and 4.	5.	6.	7.	8.
H ₂ SO ₄ ..	63·84	62·52	67·60	66·37	64·85	64·11
HNO ₃ ..	16·96	16·46	13·66	13·04	14·90	13·62
H ₂ O ..	19·20	21·02	18·74	20·59	20·25	22·27

The results with the acid ratio 1:3·8 are almost identical with those of 1:3.

When the quantity of sulphuric acid is five times that of the nitric acid, there is a rise of the nitrogen content of about 40 c.c. NO, as compared with that of the acid ratio 1:3, from which it is evident that the increased action of the sulphuric acid is somewhat limited. It is principally manifested when the ratio rises from 1:1 to 1:3.

The nitrogen content diminishes rapidly when, in an acid mixture 1:5, the ratio of cellulose to nitric acid falls from 1:30 to 1:8.

All these experiments were carried out at the temperature of the room, and the time of nitration was twenty-four hours. With nitration mixtures of ratios 1:3, 1:3·8, 1:5 respectively, nitrations were conducted at raised temperatures. After two hours' reaction at 35° the same products were obtained as with the above conditions. The nitrogen content was the same, or slightly higher.

According to the results of this section (B), the most important factor in nitration processes is certainly water. In working according to prescription to obtain a certain nitration product, the chief point to observe is that the proper proportion of water is present in the acid mixture. With regard to the amount of sulphuric acid, such accuracy is less necessary, especially with great excess of the acid, as the results are only influenced by this factor to a slighter degree.

(To be continued).

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Continued from p. 55).

Spectral Characteristics of the Plate.—If an ultra-violet plate and a very slightly sensitive silver bromide gelatin plate are exposed equally to white light it will be seen that the latter receives an impression capable of development in a far shorter time than the former, for the ultra-violet plate is very little sensitive to visible rays. This holds for the greater part of the ultra-violet spectrum. At 231 μ it begins to yield more than the gelatin plate, giving more intense and sharper images. Further on towards the shorter waves this activity increases to such a visible extent that the distribution of energy and intensity of the field between 220 and 200 μ , the reproduction of which is well known by all experimenters to lack intensity definition, undergo a complete change. All reproductions of this spectral region represent far more the absorption spectrum of the gelatin than the sensibility spectrum of the sensitive portion of the plate. It is the same with the region between 231 μ and the green part of the spectrum, where intensity and sensibility are both in an opposite sense dependent on the gelatin, which here acts as a sensitising agent, and considerably raises the sensibility of the silver bromide.

It follows from this that all measurements of light intensity, dependent on the density difference of the spectrum image, are only of relative value, and further, that they do not hold for the ordinary gelatin plate, but only for the plate formerly in use. Consequently, plates of different origin may lead to considerable variations. This fact is more important (as is generally accepted) for spectroscopy, which measures the degree of brightness of the different rays according to the degree of blackening of the lines photographed.

The ultra-violet plate can, in consequence of its sensibility, claim higher distinction than any other plate, on the one hand, for rays only to be photographed in vacuo; and on the other hand, for the uniform reproduction of the rest of the spectrum. To what extent the latter is the case may be demonstrated by spectra of the electric aluminium spark, photographed under similar conditions upon an ultra-violet plate and a gelatin dry plate respectively.

A comparison of both shows how fundamentally different are the representations of energy derived from the same source of light, how little adapted is the commercial plate to the photography of the refrangible part of the ultra-violet up to 185 μ , and how little its sensitiveness to light accords with that of pure silver bromide, which, according to earlier researches of mine, reproduces

uniformly all rays of the spectrum, from the blue portion to the smallest waves. It is further worthy of note that the extremely small quantity of gelatin used usually increases the sensitiveness of the ultra-violet plate. It is only thus possible to obtain soft half-tones in the photograph, which are not indicated by silver bromide alone.

A further advantage of the ultra-violet plate lies in its insensibility towards the diffused light of the photographic apparatus, which renders certain operations with the ordinary plate difficult in the highest degree. For example, all reproductions of the spectrum beyond $185\ \mu$ become fogged before the image has attained sufficient power, and so completely that only the most active lines remain visible. This fogging is due to the action of the rays that become scattered inside the lenses and prisms, and reach the plate as diffused light. As the diffused light consists principally of less refracted rays, *i.e.*, of rays which act more powerfully than all others on the gelatin plate, fogging is the natural result. So far, it has not been possible, for want of a suitable light-filter, to banish entirely this diffused light from the spectral apparatus, and one has to be content with diminishing it. This is attained without trouble by diminishing the amount of light passing through the slit by shortening the latter (to about $\frac{1}{2}$ m.m.) This is the only way to conduct reproductions of electric discharges above the wavelength $185\ \mu$ to the limit of ultra-violet activity of the ordinary dry plate ($182\ \mu$). The ultra-violet plate does not suffer from the diffused light because it is little sensitive to the visible and neighbouring ultra-violet rays. With this, therefore, the length of the slit may be regulated at will without the fear that length of exposure will cause fogging.

(To be continued).

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.*

By FRANCIS C. PHILLIPS.

WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is seen to consist of very fine indistinct crystals.

If the liquid containing the precipitate is heated, the precipitate re-dissolves, giving a liquid of a bright orange colour. On cooling, this solution deposits orange coloured needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air, and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

An analysis of the crystals was made in the following manner:—

A portion of the substance was dissolved in water, and a current of carbon monoxide passed through the solution, which was kept upon a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finally divided palladium could be thus easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralised by zinc, and the chlorine then determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidise the sulphur of the compound to sulphuric acid by fusion with various mixtures of alkaline carbonate with nitrate and

chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilisation. Heating with nitric acid in a sealed tube failed to yield complete oxidation, even at temperatures which involved danger to the tube. The ordinary reagents which might be looked to for the conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner:—The substance contained in a porcelain boat was placed in a porcelain combustion tube, which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 c.m. long, rolled tightly, and completely filling the cross-section of the combustion tube. After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 litres capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution, together with the washings of the large bottle and combustion tube, were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidised by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results:—

	Per cent.
Palladium	35.09
	35.19
Chlorine	23.75
	23.57
	23.65
Sulphur	21.57
	21.40
	21.41

The analytical results indicate for the compound the composition $\text{PdCl}_2(\text{CH}_3)_2\text{S}$, the calculated percentages in the case of such a compound being:—

	Per cent.
Palladium	35.41
Chlorine	23.46
Sulphur	21.22

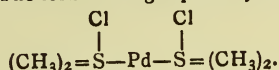
The above formula is similar to that given by Enebuske (*Journ. Prakt. Chem.*, 1888, [2], xxxviii., 358), to the compound of methyl sulphide with platinum chloride, $\text{PtCl}_2(\text{CH}_3)_2\text{S}$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide, and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, with setting free of methyl sulphide and hydrogen chloride.

One hundred grms. of water dissolved at 26.1°C , 0.15 grm. of the compound. The solution in water, and also the dry substance, possess a slight odour of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 124°C , solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something

* *Journal of the American Chemical Society*, vol. xxiii., No. 4.

of the products of its decomposition by heat. For this purpose it was heated in nitrogen. At 210° an evolution of methyl sulphide began, and continued until the temperature rose to 260° , when a black residue was left, which proved on analysis to consist of nearly pure palladium sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields up a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue.

As regards the constitution of the compound, it would seem that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written:—



This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir (*Ann. Chem. u. Pharm.*, 1853, lxxxvii., 369; *Comptes Rendus*, xxxiv., 1095), in 1853, described the compounds of methyl sulphide with mercuric chloride and iodide, and with platonic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason (*Ber. d. Chem. Ges.*, 1887, 3406), by distilling a mixture of sodium methyl sulphate with sodium sulphide.

Compound of Methyl Sulphide with Mercuric Chloride.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white colour is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in colour. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water, and more soluble in alcohol. The solution has a slight odour of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalis, and in other respects the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was $150-151^{\circ}$, but if the heat is applied more slowly, its colour grows darker, and as the result of a partial decomposition it melts at a varying and much higher temperature.

Heated in purified nitrogen it gives off methyl sulphide at about 150° , and at 170° white needle-shaped crystals form as a sublimate. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the palladium compound. Mercury

was determined by precipitation of the aqueous solution by hydrogen sulphide, and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water, and titration by silver nitrate solution. The results of the analysis are as follows:—

	Per cent.
Mercury..	64.27
	64.07
	64.19
Chlorine ..	22.26
	22.68
	22.66
Sulphur ..	6.63
	6.84
	6.76
	6.73

Other determinations were made in the case of the same compound after crystallising from alcohol. The results were:—

	Per cent.
Mercury..	64.41
	64.31
Chlorine ..	22.60
	22.53

The calculated percentages in the case of a compound having the formula $3\text{HgCl}_2 \cdot 2(\text{CH}_3)_2\text{S}$ are as follows:—

Mercury..	64.63
Chlorine ..	22.70
Sulphur ..	6.42

Loir (*loc. cit.*) assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $\text{HgCl}_2(\text{CH}_3)_2\text{S}$. Analyses have been made of many preparations of the mercuric chloride methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

(To be continued).

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.*

By A. G. WOODMAN and L. L. CAYVAN.

THE estimation of phosphates is a part of the sanitary examination of waters which has been somewhat neglected in the past, doubtless because the ordinary methods of determination are quite tedious, and because the exact significance to be attributed to the presence and amount of phosphates is a question still in abeyance. There can be no question, however, in consideration of the probable decomposition and oxidation of the organic phosphorus compounds in animal excretions, that an excessive amount of phosphates in a water, unless otherwise accounted for, is an indication of pollution. If, then, the amount could be estimated, by a method sufficiently simple and rapid, enough data might readily be gathered to render the determination of much greater value than at present. Especially would this be true in comparing several waters from the same locality.

Repeated trials of methods which have been proposed have shown that there is none which is perfectly satisfactory for accurate and rapid work. The extremely small quantities of phosphate found even in polluted waters would seem to preclude the use of gravimetric methods. Such methods, however, have been used. Hehner (*Analyst*, iv., 23; and v., 135), and also Harvey (*Analyst*, 1880, 197), concentrate a large quantity of the water and determine the phosphate gravimetrically as ammonium phosphomolybdate. All gravimetric methods are objectionable on account of the time required. Furthermore, not being very delicate, they necessitate considerable con-

* Contributions from the Laboratories of the Massachusetts Institute of Technology. From the *Journal of the American Chemical Society*, xxiii., No. 2.

centration, which, as will be shown later, almost invariably occasions a loss of phosphate. Phipson (CHEMICAL NEWS, lvi., 251) precipitates the phosphate from a large volume of water by means of alum and an excess of ammonia, making the final precipitation with ammonium molybdate. The process is a long one, and experiments with a more delicate method showed that the precipitation of the phosphate is not complete.

On the whole, the colorimetric methods seem best adapted for the determination. Several such methods have been proposed, based on the colour given to dilute phosphate solutions by ammonium molybdate in the presence of nitric acid. Lepierre (*Bull. Soc. Chim.*, 1896, xv., 1213) evaporates a litre of water, dehydrates the silica by repeated evaporations with nitric acid, ignites strongly, and filters. The phosphate in the filtrate is estimated colorimetrically by ammonium molybdate. Jolles and Neurath (*Monatshefte*, 1898, xix., 5) use potassium molybdate instead of the ammonium salt, and Jolles (*Archiv. f. Hygiene*, 1899, xxiv., 22) has applied the method to the determination of phosphoric acid in water, removing the silica from the residue obtained by the evaporation of a litre of water by ignition at 130°C. These methods are open to the same objections as the gravimetric methods, namely, that by requiring the evaporation of large quantities of water, they introduce serious liability to error and are too tedious to be of general use. Furthermore, the temperature at which the residue should be ignited to remove silica is a matter of importance, especially when dealing with small amounts. In view of these considerations, it was deemed advisable to make a critical study of the colorimetric methods.

Apparatus and Reagents.

Ammonium Molybdate.—50 grms. of the pure neutral salt were dissolved in a litre of distilled water.

Nitric Acid (sp. gr. 1.07).—Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution.—0.5324 grm. of pure crystallised sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) was dissolved in freshly distilled water, 100 c.c. of nitric acid (1.07) added, and the whole diluted to 1 litre. This solution is diluted to make the standards. 1 c.c. = 0.0001 grm. P_2O_5 . The solution keeps without change for several months if preserved in well-stoppered bottles of hard glass; after a longer time it becomes slightly stronger, owing to the silica dissolved from the glass.

Standard Silica Solution.—About 5 grms. of precipitated and washed silica were dissolved in an excess of sodium hydroxide made from metallic sodium. The solution was made faintly acid with nitric acid, diluted to a definite volume, and the silica determined in an aliquot part. The standard solution was made by diluting this strong solution until 1 c.c. = 0.001 grm. SiO_2 .

It was found that sodium or potassium molybdate offered no particular advantages over the ammonium salt. The colour obtained was no more intense and was distinctly greener, which made the reading of the standards much more difficult. It was found also that for a given amount of the phosphate solution the depth of colour and the rapidity with which it developed depended to a certain extent upon the quantity of reagents used. The best results were obtained by the use of 4 c.c. of the ammonium molybdate solution and 2 c.c. of the nitric acid.

For comparing the colours the ordinary Nessler tubes were used at first, but it was found that if tubes of too small diameter were used the colours were not easily read; if of too large diameter the delicacy of the reaction is considerably decreased. The tubes which have been found most satisfactory have a capacity of 100 c.c. They are of hard white glass, about 2.5 c.m. in diameter and 24 c.m. long to the 100 c.c. mark. The colour is a rather difficult one to read closely, and for very accurate readings probably some form of colorimeter could be used to advantage. For any but the most refined work, however, it will be found amply sufficient to compare the tubes by

a north light against a reflecting white surface, such as a pure white unglazed porcelain tile supported at an angle of about 40°. This procedure was followed in all this work, and was found most practical where a number of tubes are to be compared rapidly.

Using no greater precautions than those just described, the delicacy of the test is considerable. If care is taken to choose two tubes, identical in all respects, it is possible to detect 0.002 c.c. of the standard phosphate solution in 50 c.c. of water. If the tubes are heated to 60°C. 0.001 c.c. can be read. The delicacy of the reaction is therefore sufficient to show the presence of 1 part of phosphate as P_2O_5 in 500,000,000 parts of water. On the other hand, comparatively large quantities of phosphate may be present in 50 c.c. of water, without causing precipitation or turbidity on the addition of the reagents except after standing a considerable time. On account of the difficulty in matching the more intense colours, no higher standard than 10 c.c. of the standard solution in 50 c.c. of water is ever used, and it has been determined by direct experiment that a standard as high as this will not become turbid at room temperature for twelve or fifteen hours. The colour of the phosphate standard is an additive property; it makes no difference apparently whether the higher standards are made up directly or by the addition of more of the standard solution to the lower standards.

The question of the permanency of the phosphate standards was one of the first ones investigated. Lepierre, in the article previously cited, stated that the phosphate standards can be preserved for several months without change. Careful comparison of a number of standards from day to day, however, showed that this was not strictly true. The change in some of the higher standards, while slight, was still distinctly noticeable when carefully observed, and in others, especially the lower ones, the colour faded so much in two or three days that the standards were rendered useless. Nor was any other substance found giving the right colour which was suitable for the preparation of permanent standards. The most satisfactory was a dilute solution of picric acid, which gave a yellowish green colour very similar to the phosphate colour. But it was found impossible to keep even these standards in glass tubes, since the solvent action on the alkali of the glass was sufficient to form a slight amount of the alkali picrate, which has a more intense colour than the picric acid itself; hence, the standards slowly increased in colour. The attempt was therefore abandoned, and fresh phosphate standards were used for all comparisons.

Study of the Phosphate Reaction.

For a given volume of water and a definite amount of reagents the depth of the phosphate colour is a function of two factors, namely, the amount of phosphate present and the temperature. To determine the exact effect of the latter for the conditions employed in this work, readings of various phosphate standards were made at different temperatures. Differing amounts of the standard solution were diluted to 50 c.c., and, after the addition of the reagents, were heated gradually in a water-bath from 20° to 60°C. Readings were taken every 5°. If the reagents are added after heating, the colours are not so clear. The heating was not carried beyond 60°, because above this temperature the standards become cloudy and the higher standards tend to precipitate. The maximum colour is given between 90° and 100°, but the tendency to precipitation renders the reading at this temperature impracticable. The most satisfactory colours are obtained at 20–30°, practically at room temperature. A variation of a few degrees causes only a slight error. The results are given in the accompanying table.

The results shown graphically show slight irregularities, due to the difficulty of reading exactly. The increase in colour with increased temperature is considerable, double in the higher standards. All of the standards on cooling go back to less than their original colour. No case of

Amounts phosphate added.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.
6 c.c. ..	6'2 6'2 6'2	7'2 7'2 7'7	7'7 7'8 8'2	8'2 8'3 9'0	8'7 8'7 9'2	9'6 10'2 9'7	— 10'4 10'4	10'2 10'7 10'3
Average ..	6'2	7'3	7'6	8'5	9'0	9'8	10'4	10'5
5 c.c. ..	5'1 5'1 5'1	5'9 5'3 5'2	6'6 6'1 6'3	7'3 7'2 7'1	7'8 7'9 8'0	8'0 8'4 8'3	8'6 8'6 8'7	9'6 9'4 8'9
Average ..	5'1	5'5	6'4	7'2	7'9	8'3	8'6	9'2
4 c.c. ..	4'1 4'1 4'1	4'7 4'8 4'8	5'1 5'1 5'1	5'4 5'5 5'5	6'4 6'4 6'4	6'6 6'5 6'6	6'9 6'8 7'0	7'1 7'3 7'4
Average ..	4'1	4'7	5'1	5'5	6'4	6'6	6'9	7'2
3 c.c. ..	3'1 3'4 3'2	3'4 3'7 3'7	3'9 4'4 3'9	4'5 4'7 4'3	5'1 5'2 4'9	5'7 5'3 5'4	5'8 5'7 5'5	6'2 5'9 6'2
Average ..	3'2	3'6	4'1	4'5	5'1	5'5	5'7	6'1
2 c.c. ..	2'2 2'2 2'4	2'5 2'5 2'6	2'7 2'8 2'9	2'9 3'1 3'0	3'1 3'2 3'3	3'4 3'4 3'4	3'6 3'7 3'5	3'9 3'9 3'9
Average ..	2'2	2'5	2'8	3'0	3'2	3'4	3'6	3'9
1 c.c. ..	1'1 1'1 1'1	1'2 1'2 1'2	1'4 1'3 1'4	1'5 1'4 1'5	1'5 1'5 1'5	1'7 1'7 1'5	1'9 1'8 1'7	1'9 1'8 2'0
Average ..	1'1	1'2	1'4	1'4	1'5	1'6	1'8	1'9
0'7 c.c. ..	0'75 0'75 0'75	0'80 0'80 0'80	0'85 0'85 0'83	0'95 0'90 0'95	1'1 1'05 1'05	1'2 1'15 1'15	1'25 1'25 1'20	1'27 1'28 1'25
Average ..	0'75	0'80	0'85	0'93	1'05	1'17	1'22	1'26
0'5 c.c. ..	0'60 0'60 0'60	0'65 0'60 0'65	0'70 0'65 0'70	0'80 0'75 0'75	0'90 0'85 0'85	0'95 0'90 0'85	1'05 0'95 0'95	1'10 0'95 0'95
Average ..	0'60	0'65	0'70	0'77	0'87	0'90	0'98	1'01
0'4 c.c. ..	0'45 0'45 0'45	0'50 0'55 0'55	0'55 0'55 0'55	0'65 0'57 0'58	0'70 0'60 0'65	0'75 0'65 0'67	0'80 0'70 0'70	0'80 0'70 0'70
Average ..	0'45	0'53	0'55	0'60	0'65	0'68	0'72	0'72
0'3 c.c. ..	0'33 0'33 0'33	0'36 0'36 0'36	0'39 0'39 0'39	0'44 0'45 0'44	0'48 0'50 0'54	0'58 0'55 0'58	0'63 0'60 0'60	0'68 0'65 0'65
Average ..	0'33	0'36	0'39	0'44	0'51	0'57	0'61	0'66
0'2 c.c. ..	0'23 0'23 0'23	0'27 0'27 0'27	0'31 0'30 0'30	0'32 0'33 0'33	0'34 0'33 0'34	0'37 0'36 0'37	0'38 0'38 0'38	0'39 0'39 0'39
Average ..	0'23	0'27	0'30	0'33	0'34	0'37	0'38	0'39
0'1 c.c. ..	0'11 0'12	0'13 0'13	0'14 0'14	0'16 0'16	0'17 0'17	0'18 0'18	0'19 0'19	0'20 0'20
Average ..	0'11	0'13	0'14	0'16	0'17	0'18	0'19	0'20

Several of the methods previously proposed for the determination of phosphates involve the concentration of the water, followed by heating at various temperatures. Preliminary experiments had shown the liability to loss during such procedure, and the point was further investigated. One litre of water, containing 5 c.c. of phosphate solution and 2 c.c. of nitric acid, was evaporated to dryness; a loss of 16 per cent of the phosphate occurred. Phosphate standards made up in a volume of 50 c.c., with varying amounts of nitric acid, were evaporated to dryness, and some of them heated in an air-bath at 100° for periods varying from fifteen minutes to two hours. A loss of phosphate always occurred whether done in platinum or porcelain dishes. Other standards were evaporated and heated at 135° C., still others were ignited over a free flame; a loss was found in all cases. An idea of the magnitude of the loss may be gained from the following figures:—

Evaporated without Nitric Acid and Heated One Hour at 100°.

In porcelain dishes—								
Amount added ..	0'1	0'2	0'5	1'0	2'0	5'0		
Amount found ..	0'1	0'18	0'45	0'75	1'8	4'9		

In platinum dishes—								
Amount added ..	0'1	0'2	0'5	1'0	2'0	5'0		
Amount found ..	0'07	0'12	0'4	0'85	1'8	4'9		

Evaporated as above, but Heated One Hour at 135°.

In porcelain dishes—								
Amount added ..	0'1	0'2	0'5	1'0	2'0	5'0		
Amount found ..	0'0	0'0	0'0	1'0	1'5	4'0		

In platinum dishes—								
Amount added ..	0'1	0'2	0'5	1'0	2'0	5'0		
Amount found ..	0'0	0'0	0'1	0'6	1'3	2'7		

In all cases where nitric acid was used and the residue was heated at 100°, the loss on a 2 c.c. standard was from 0'02 to 0'22 c.c. greater the more acid used. Where the ignition was made over a free flame the loss varied from 25 to 50 per cent, highest in the low standards. Without the addition of nitric acid the loss on evaporation was very irregular. In the presence of a definite quantity of acid the loss was more nearly constant. Without going into great detail, it may be said that it was apparent that the loss was due to some change taking place while the solution is dilute and hot. The total loss occurs usually during the concentration of the solution to one-half its volume.

(To be continued).

CORRESPONDENCE.

THE SOUTH AFRICAN COLLEGE.

To the Editor of the Chemical News.

SIR,—With reference to a paragraph in your issue of April 26 (CHEM. NEWS, lxxxiii., 194), wherein you incidentally observed that Mr. R. T. Smith, B.A. (Cantab.), recently appointed Principal of the Northern Polytechnic Institution, "organised and equipped the South African College at Cape Town, and acted as Professor of Mathematics and Physics in the College for some years," I am asked by the Council of the College to inform you that the South African College was founded over seventy years ago—in 1829.

A few years ago a Laboratory for Experimental Physics was erected in connection with the Institution, and on the Building Committee, of which I had the honour of being Secretary, Mr. Smith, then recently appointed Professor of Physics, naturally occupied a most important advisory position. It is not correct to say that Mr. Smith was "Professor of Mathematics and Physics in the College." During the whole of Mr. Smith's tenure of office as Professor of Physics the mathematical chair was occupied

precipitation occurred, although some of the highest standards were too turbid to be read easily.

by the late Professor Francis Guthrie, B.A., LL.B., brother of the distinguished chemist the late Frederick Guthrie.—I am, &c.,

CHAS. F. JURITZ, M.A. (Senior Govt. Analyst),
Hon. Sec. S.A. College Union.

Government Analytical Laboratory,
Cape Town, Cape of Good Hope,
July 10, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 3, July 15, 1901.

Thermometric Examination of Solid Potassium Hydrates.—M. de Forcrand.—The author's researches show that, besides the two compounds KOH and $\text{KOH} + 2\text{H}_2\text{O}$, there exist two intermediate hydrates, $\text{KOH} + 0.5\text{H}_2\text{O}$ and $\text{KOH} + \text{H}_2\text{O}$. The possible hydrates, $\text{KOH} + 0.25\text{H}_2\text{O}$ and $\text{KOH} + 1.5\text{H}_2\text{O}$, also are on the straight lines joining neighbouring points. The heat of fixation of $0.5\text{H}_2\text{O}$ liq. on to solid KOH is $+6.30$ cal., or $+12.60$ calories per molecule. The fixation of a second half molecule of water whilst passing to the compound $\text{KOH} \cdot \text{H}_2\text{O}$ only evolves $+3.15$ calories, or $+6.30$ calories per molecule. Finally, the heat evolved for the fixation of the entire molecule on to $\text{KOH} \cdot \text{H}_2\text{O}$ to give $\text{KOH} \cdot 2\text{H}_2\text{O}$ is only $+3.04$ cal. The three numbers $+12.60$, $+6.30$, and $+3.04$ are exactly in the proportion $4:2:1$. These facts explain why potash, when used to absorb water (from gases, for instance), should be in the form KOH; specimens of commercial "pure potash" usually have about the composition $\text{KOH} + \text{H}_2\text{O}$, and are therefore very imperfect dehydrating agents. Apparently the first portions of water fixed (up to $0.25\text{H}_2\text{O}$) evolve less heat than the following portions (from 0.25 to $0.50\text{H}_2\text{O}$).

Iodine-phenyl Ethereal Derivatives.—P. Brenans.—In a previous paper the author relates the conditions under which iodine gives with phenol the di-iodophenol, $\text{OH}-\text{C}_6\text{H}_3-\text{I}_2$, 1.2.4, and the tri-iodophenol, $\text{OH}-\text{C}_6\text{H}_2-\text{I}_3$, 1.2.4.6. He now describes the methods of preparation and the properties of a number of ether oxides and ether salts obtained from these two iodine compounds—(1) Ether oxides of di-iodophenol, e.g., propylphenylic, isopropylphenylic, and allylphenylic ethers; (2) ether oxides of tri-iodophenol, e.g., tri-iodoanisole, tri-iodophenethole, propylphenylic, allylphenylic, and benzylphenylic ethers; (3) ether salts of di-iodophenol, e.g., neutral succinic and neutral phthalic ethers; (4) ether salts of tri-iodophenol, e.g., acetic ether and benzoic ether.

Action of Pyridic Bases on the Tetrahalogen Benzoquinones.—Henri Imbert.—When some acetic ether is placed in a flask with a reflux condenser, and, on bringing this to boiling-point, chloranile is added with some pyridine, the liquid first becomes red, then a reaction begins; acetic acid is added, and a red body is obtained from this mixture which apparently has the formula $\text{HO}-\text{C}_5\text{H}_2\text{N}=\text{C}_6\text{Cl}_2\text{O}_2$.

New Decompositions of Methyl-*c*-butyrylacetylacetate.—A. Bongert.—In a recent paper the author explained the action of hydrazine on *o*- and *c*-methyl butyrylacetylacetate. Having had occasion to re-examine the reaction on the latter body, he was surprised to find that he obtained totally different results. The varying reactions were due to the fact that in the first experiments he employed hydrazine in the form of acetate, obtained by double decomposition between its sulphate and sodium acetate in very dilute solution. In the second experiment, the action took place between an aqueous solution of hydrazine hydrate and butyrylacetylacetate dissolved in ether.

Pyromucic and Isopyromucic Acids.—M. Chavanne.—Besides pyromucic acid, Limpricht found in the dry distillation products of mucic acid a new acid, isopyromucic acid, which he distinguished by the green colour which it gives with ferric chloride. The author undertakes an examination of the properties of these bodies. The first experiments resulting in a method of sharply distinguishing between the two acids, and a method of separating the isopyro- from pyromucic acid.

Dichlor-orthoxylenes.—L. Ferrand.—By the action of chlorine on orthoxylene in presence of iodine, Claus and Kantz obtained a little of the mono- and trichlor-orthoxylenes and some 4-5-dichloro-orthoxylylene in the form of a liquid boiling at 227° . This liquid, when oxidised by dilute nitric acid, gives an acid which seems to be 4-5-dichlorophthalic acid, because, if distilled with soda-lime, it gives ortho-dichlorobenzene, which melts at 183° . They also obtained, as well as this liquid compound, a certain quantity of a solid isomer fusing at 73° , which they did not examine. The author continues these researches, and determines the composition of this isomer, but finds, when employing the same method as that used by Claus and Kantz, he obtains two isomers—one a liquid, dichlor-metaxylylene, boiling at 221° ; and the other a solid (melting-point 68°). His researches apparently show that, during the action of chlorine on orthoxylene in the presence of iodine, the three possible chlorine derivatives are obtained, and not only one as Claus affirmed.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sympathetic Ink.—I remember reading somewhere of a certain compound which could be used as ink. Its peculiar property was that it faded out as soon as it got dry, and could only be read when dampened. I have seen this done by friends and have used the fluid myself. I do not think it had anything to do with litmus or the commoner colouring matters. It must have been easy to prepare since we students could make it. If anyone can tell me how it could be done I shall be very much obliged.—W. H. S.

BIRKBECK INSTITUTION,

Breams Buildings, Chancery Lane, E.C.

LECTURES AND PRACTICAL WORK in—

CHEMISTRY .. J. E. MACKENZIE, Ph.D., D.Sc.

PHYSICS .. A. GRIFFITHS, D.Sc.

METALLURGY.. G. PATCHIN, A.R.S.M.

DAY CLASSES.—

CHEMISTRY—Tuesday, Thursday, Saturday, 10—1.

PHYSICS—Monday, Wednesday, Friday, 2.30—5.30.

METALLURGY—Monday, Wednesday, Friday, 10—1.

EVENING CLASSES in all subjects.—

Every Evening except Saturday, from 6 p.m.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 30th; Lectures begin October 8th, 1901.

Hostels for Men and for Women Students.

Prospectuses on application to the SECRETARY.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2177.

PRELIMINARY NOTE ON A POSSIBLE METHOD OF ATTAINING THE ABSOLUTE ZERO OF TEMPERATURE.

By GEOFFREY MARTIN.

THE conception of an absolute zero of temperature belongs to the nineteenth century. Previously such an idea existed only as a vague speculation.

The magnificent researches of Andrews, Cailletet, Pictet, and others on the permanent gases brought home to all this possibility in a forcible manner. Men heard with amazement that air had been reduced to a mobile liquid so intensely cold as to burn like molten lead; and for the first time they caught a glimpse of a strange cold world with its mystery and possibilities—a world hitherto scarce dreamt of.

Matter without heat! The idea seemed almost absurd to the general public. Yet towards the end of the last century scientists were rapidly reducing it to that condition. Oxygen, air, nitrogen, all were liquefied successively, and a temperature less than 100° C. from the absolute zero was obtained. Hydrogen barred the way for a long time, and it was not until 1898 that Dewar obtained it in quantity as a beautiful, clear, colourless liquid, possessing a density only one-fourteenth that of water at 0° C. By rapidly evaporating it he obtained a temperature only $13-14^{\circ}$ C. from the absolute zero itself—a notable achievement.

By the use of liquid helium a still lower temperature will be probably obtained, but the absolute zero itself is not attainable by such methods, for even the most volatile gas will become solid and lose all vapour tension long before this point is reached. Some other method of making matter yield up its energy must therefore be devised.

Perhaps the phenomena of thermo-electricity will be of use. Peltier showed that if a current be passed across an antimony-bismuth junction in one direction heat is developed, and in the reverse heat is absorbed, and an appreciable cooling effect obtained. Similarly in the case of any two other metals heat is generated if the current traverses the surface of contact in one direction, and is consumed if it passes in the opposite direction—the quantity of reversible heat being in each case proportional to the strength of the current, and to a coefficient π depending on the nature of the metals and their temperature.

So that, in general, if r is the resistance of the part of the circuit containing the junction, the energy converted into frictional heat is c^2rt , and the energy converted into reversible heat is $c\pi t$. Hence, if H be the quantity of heat produced in t secs., we have $J. H. = c\pi t + c^2rt$. By making a small hole at the junction of a bismuth and antimony bar, in which was placed a drop of water and a small thermometer, the whole being cooled to zero, Lenz found that when a current was passed from bismuth to antimony the water was frozen, and the thermometer sank to -3.5° C.

Opposing this fall in the junction's temperature there are in general two influences.

Firstly, when a current is passed through a conductor a frictional generation of heat occurs, which tends to mask the cooling effect. Secondly, when one part of a circuit is at a much lower temperature than the other parts, heat will flow by conduction from the hotter to the colder parts, and thus again oppose further cooling.

When a stationary low temperature has been reached by the junction, we must imagine that as much heat is absorbed by the current in unit time as is imparted to the junction by means of both of those influences I have mentioned working together.

If, therefore, we could diminish or do away with these, a very great cooling effect could be obtained.

The frictional heating could be eliminated to a great extent by cooling the whole to the lowest temperature attainable by the use of liquid hydrogen. Recent experiments by Profs. Fleming and Dewar show that an astonishing fall in the specific resistance of most metals takes place at very low temperatures. Thus, the specific resistance of copper and iron fall from 1564 and 9115 respectively at 0° C., to 289 and 1200 at -205° C.; while at a temperature only 20° lower these numbers become 144 and 660—i.e., the specific resistance at -220° C. is actually half that at -200° C. (*vide* Foster and Atkinson's "Electricity and Magnetism," 1896, p. 162). Such an enormous diminution in the specific resistance leads one to expect that at only $13-14^{\circ}$ C. from the absolute zero—the lowest temperature yet attained by Dewar—the resistance would be practically negligible, so that the term c^2rt in the above expression would become extremely small, even when currents are employed considerably more powerful than those which can be used at ordinary temperatures for producing the Peltier effect. If the quantity π remained appreciably large it is quite possible that matter could by such means be chilled almost to the absolute zero without the masking effect of frictional heat becoming sensible.

The second influence, namely, the flow of heat by conduction from the hotter parts of the bar to the cold junction, could be eliminated by avoiding a sensible temperature difference between the chilled junction and the rest of the circuit. For instance, each small section of the main circuit could be cooled simultaneously with the junction by means of a number of other chilled thermo-electric junctions. By the use of some such contrivance the temperature of the junction need never become very much lower than that of the rest of the circuit. The coefficient π would certainly alter with the temperature. Unless it completely vanished for all bodies at very low temperatures such an effect could be corrected by properly choosing the metals forming the junctions.

At the absolute zero molecular motion has completely died away; matter even in this condition is not the cold dead mass it is sometimes pictured to be, but is still quivering with motion. Each individual atom is itself a seething universe of still smaller particles, as has been demonstrated by J. J. Thomson's work on Ions. The emanations from radio-active matter have also proved to be particles enormously smaller than atoms, shot forth from the molecule with a velocity of many tens of thousands of miles a second.

At the absolute zero all that has occurred is a disappearance of relative motion among the particles of matter of a molecular scale of magnitude.

For vastly smaller and vastly greater particles, relative motion or "temperature" still exists. It is this latter property that will make the attainment of the absolute zero such a vitally important achievement. For it is only in matter in this condition that we can study internal atomic vibrations free from secondary disturbances caused by the approach and recedence of neighbouring atoms.

The measurement of the molecular refraction, dispersion, rotation of the plane of polarisation, and other similar constants for different chemical compounds when reduced to this condition, will certainly lead to most important discoveries regarding the structure of atoms and molecules.

For it is only when all bodies are in such a state that the full atomic effect of each atom in a molecule, unmasked by artificial clashing and jarring, can be obtained.

Bristol, August 3, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Continued from p. 64).

Pyritic Ores (continued).

Method (b).—The oxidation of the pyritic material in an ore by the use of nitre during fusion is preferred by some assayers, as it is somewhat more expeditious than oxidation by roasting. The method, however, is limited in its application to gold ores, as the use of large quantities of nitre is to be deprecated, since the contents of the crucible are very liable to boil over owing to the energetic effervescence which takes place.

Ores consisting chiefly of pyritic material frequently require more than twice their own weight of nitre to effect complete oxidation; and as it is generally necessary, in the case of gold ores, to use from 30 to 50 grms. of ore for assay, the use of nitre becomes impracticable.

If nitre is employed for effecting the oxidation of pyritic material the approximate quantity needed is ascertained by the methods subsequently given for the assay of antimonial ores by this process, and the remarks on the use of nitre there given are equally applicable to pyritic ores.

The approximate quantity of nitre necessary to oxidise various "sulphurets" has been arrived at by experiment, and is given in the following table:—

Approximate Oxidising Effect of Nitre.

	Parts of nitre required to one part of "of sulphuret."
Iron pyrites	about 2 to 2½ parts
Mispickel	
Copper pyrites	" 1½ to 2 "
Fahlerz	
Zinc blende	
Antimonite	" 1½ "
Galena	" 3 "

When the nitre has completed its action the product consists mainly of metallic oxides, and the ore is fluxed accordingly on the lines indicated for basic ores.

Method (c).—Fusion of gold ore with lead oxide alone is adopted by some assayers in cases where the sample to be operated upon contains only an amount of pyritic material sufficient to yield a convenient quantity of lead for cupellation. When this method is used the lead oxide must be in excess, as it not only serves as an oxidising agent, but also acts as a flux for the gangue of the ore and the oxides resulting from the oxidation of the pyritic material. Silica requires nearly 5 parts of litharge, and the metallic oxides require from 2 to 10 parts to form fusible compounds. In this case, which applies to ores containing about 10 per cent or less of pyritic material, a charge of from 30 to 50 grms. of ore is usually employed, and is fused with from four to five times its weight of red-lead or litharge. Charcoal powder is added in cases where the proportion of sulphides is not sufficient to give the required weight of lead. Red-lead is used in preference to litharge on account of the larger amount of oxygen it contains.

As the quantity of lead oxide requisite for the decomposition of a sulphide is considerable, very pyritic ores cannot be conveniently assayed by this method unless sufficiently rich to allow of comparatively small quantities of material being operated upon. The proportion of lead oxide required to effect complete desulphurisation varies according to the nature of the sulphide, but in all cases is large. When less than the requisite quantity of lead oxide is used, only a portion of the sulphide is decomposed, and a corresponding quantity only of lead reduced, whilst the remainder of the sulphide forms, in combination with the litharge and metallic oxide which is produced, a compound belonging to the class of oxysulphides which are

generally very fusible (Mitchell). If oxysulphides are present to a large extent in the slag they cause the retention of appreciable quantities of the precious metals.

All sulphides, arseno-sulphides, &c., are readily oxidised by lead oxide with the production of a quantity of lead equivalent to the oxidisable substances present; this method of assay is therefore inconvenient on account of the large quantity of lead it produces, which needs to be reduced by scorification before it can be cupelled. The method may be modified in some cases by adding a little nitre to the mixture to assist in oxidising the sulphur, &c. One grm. of nitre is equivalent in oxidising effect to 20 grms. of red-lead or 26 grms. of litharge.

Method (d).—In this method metallic iron is used as a desulphurising agent, the iron combining with the sulphur to form ferrous sulphide, which passes into the slag. ($\text{FeS}_2 + \text{Fe} = 2\text{FeS}$).

The method can only be satisfactorily applied to ores containing not more than about 25 to 30 per cent of pyrites. When the percentage of pyrites is much above this the results obtained are far from trustworthy, and the method cannot be recommended. A moderate quantity of sulphur may be successfully converted into iron sulphide and dissolved in the slag, but with ores containing excess of pyrites it is difficult to effect complete reduction by this method, even when large quantities of metallic iron are added to the charge; the lead button obtained is always more or less brittle, owing to the presence of sulphur, and is frequently accompanied by a layer of regulus. In cases where a regulus is produced it is best to repeat the assay by the method of oxidation by roasting previous to fusion.

The following quantities are convenient for ores containing 30 per cent of pyrites or less:—

Ore	50 grms.
Red-lead	40 to 50 "
Charcoal powder	2 to nil "
Borax	10 to 15 "
Sodium carbonate	40 to 50 "

With the addition of metallic iron.

The slags should be strongly alkaline, and to secure this end an excess of sodium carbonate should be employed in the charge.

To ensure the complete collection of the precious metals a comparatively large button of lead should be obtained from the fusion. From the charge given, a lead button would be obtained weighing from 30 to 40 grms.

The fusion should be performed at a comparatively low temperature, and the crucible should remain in the furnace for about five minutes after the contents are in tranquil fusion. The iron is then taken out and examined while hot, and should any shots of lead be found adhering to it, they must be washed off by immersing it in the molten slag, after which it is withdrawn, and the crucible is left in the furnace for a few minutes longer. The crucible is then removed from the furnace, and its contents poured into a mould in the ordinary way. When arsenic is present the iron will decompose the arsenical compound with the formation of a speiss, which separates as a hard greyish-white layer on the surface of the button of lead. The separation of a small quantity of speiss may be disregarded, as it seldom retains an appreciable quantity of gold, but if large quantities of arsenic are present, it must be eliminated by previously roasting the ore with the precautions mentioned in the treatment of arsenical ores described subsequently.

Hard and somewhat brittle lead buttons will be obtained from ores containing copper sulphides, as these compounds are partially reduced to the metallic state by iron and lead, the copper passing into the lead button, and causing trouble in the cupellation unless previously removed by scorification. In this case a cupriferous regulus, which retains appreciable amounts of gold and silver, is also frequently formed. Ores containing much copper or antimony must be treated by special methods described

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

subsequently. The presence of antimony compounds will produce brittle lead buttons, and give rise to the formation of a scoria on the cupel, which tends to retain part of the precious metals and leads to unsatisfactory results.

Arsenical Ores.—Arsenic is most frequently associated with gold ores as mispickel (arsenical pyrites), and occasionally as oxides.

Its presence gives rise to the production of compounds which tend to diminish the accuracy of the assay. It is therefore necessary to eliminate the arsenic, and this is usually effected by roasting or by the use of nitre. Much diversity of opinion exists as to which is the better of these two methods, many assayers hesitating to roast arsenical ores on the ground that, owing to the volatile character of arsenic, mechanical loss of the precious metals is caused. It has been pointed out that this may occur when too high a temperature is employed at the outset, thus causing a rapid disengagement of the volatile constituents of the ore, but with due precaution this may be avoided. The formation of arseniates is mostly to be feared, as they are liable to remain undecomposed, and cause loss of gold and silver in the slag during fusion. The ore is roasted, with all the precautions previously mentioned under pyritic ores, until completely oxidised; then from 5 to 10 per cent of charcoal powder is added, and the roasting continued until all the carbon is burnt out. Owing to the rapidity with which arsenic vapourises, great care is needed in regulating the temperature.

An attempt to eliminate arsenic by rapid oxidation would be attended with the danger of converting it into arseniates of the metals present in the ore, such as iron, copper, lead, &c. When once formed, arseniates are not readily decomposed, as they resist a high temperature, and are only slowly converted into sulphates at a red heat by the sulphuric acid formed during the later stages of the roasting.

The product obtained by roasting the ore is composed largely of ferric oxide, and is fluxed according to the directions given for the treatment of basic ores. When the oxidation of the arsenical compounds is effected by means of nitre, the ore may be treated by the nitre methods described under "Antimonial Ores."

(To be continued.)

CRITICAL REMARKS ON M'KENNA'S METHOD OF ANALYSIS OF TUNGSTEN AND CHROME STEELS. THE DETERMINATION OF TUNGSTIC ACID AND SEPARATION FROM SILICA.*

By OTTO HERTING, Philadelphia.

In the *Proceedings of Engineers' Society of Western Pennsylvania*, 1900, xlvii., p. 1186, the "M'Kenna Method of Analysis of Chrome and Tungsten Steels" was described in the form of an abstract from the *CHEMICAL NEWS*, lxxxii., 67. That this method leads to incorrect results in the cases of silicon, sulphur, and tungsten, I will attempt to prove, and, at the same time, give the methods by which correct results may be obtained.

As regards the determination of silicon, Mr. M'Kenna seems to be unaware that, by the solution of an iron containing silicon in hydrochloric acid, there is always volatile SiH_4 formed; hence the silicon determination comes out too low. Every iron and steel chemist always uses nitric acid, or nitric acid and sulphuric acid, to dissolve when silicon is to be determined.

The determination of sulphur, which M'Kenna unites with that of silicon, must also lead to incorrect and low results, which I have already proven in the article, "The Useful Methods for the Determination of Sulphur in Iron

Pyrites," &c. (*Chem. Ztg.*, 1899, 23—25). In this article, based on the classical works of Campredon and Schulte (*Stahl in Eisen*, 1897, No. 12), I have maintained:—"All methods which rest on the evolution of H_2S give too low results, unless a combustion tube heated to a low red heat is interposed." These articles have not been reproduced in the *CHEMICAL NEWS*, and for this reason, therefore, have probably not come to the knowledge of Mr. M'Kenna.

For the analysis of tungsten iron alloys, the exact determination of tungsten and the separation from silica is of the greatest importance. As regards the separation from SiO_2 of WO_3 I can maintain, on the ground of many experiments which I have made with quantitative mixtures of pure tungstic acid and pure ignited silica, that the methods given in the text-books, which rest on the volatilisation of SiO_2 by HFl , are incorrect. There must be formed by the ignition of tungstic acid and silica a silico-tungstic acid, which, treated with HFl , is volatile.

For the analysis of a ferro-tungsten I use the following method:—1.0 to 3.0 grms. of the sample is treated with aqua regia, evaporated to dryness twice on the water-bath with HNO_3 , dried at 120° , taken up with dilute HNO_3 , filtered, and washed with the same dilute acid; there remains insoluble $\text{WO}_3 \cdot \text{SiO}_2$, together with a little iron. In order to remove the latter the residue is fused with Na_2CO_3 , taken up with water, the iron filtered off (this is afterwards examined for silica); the filtrate is evaporated to dryness twice with HNO_3 , taken up with dilute HNO_3 and filtered. The residue, consisting of SiO_2 and WO_3 , is ignited and weighed, then carefully fused with five times its weight of KHSO_4 , and the fusion digested with a weak ammonium carbonate solution, whereby the WO_3 goes into solution, and a smooth separation is obtained.

Certainly, this method requires much time, but it gives satisfactory results.

In conclusion, I would like to mention that, while Mr. M'Kenna dissolves so readily tungsten chrome iron alloys in acids, I have never been able to do this with chrome alloys. I have always had to make a fusion with sodium, potassium carbonate, and magnesia.

As regards the chrome determination which M'Kenna mentions, the same is already fully described in Ledebur's "Leitfaden für Eisenhüttenlaboratorien," 1895, p. 36.

It would please me much if these lines should cause more study of the "Action of Hydrofluoric Acid on Tungstic Acid in the Presence of Silica."

A REPLY TO THE ABOVE.

By A. G. M'KENNA,

IN the seventh number of the *Zeitschrift für Angew. Chemie* appears the above somewhat caustic criticism by Mr. Herting, of Philadelphia, on the method I use in analysing chrome and tungsten steels, described by me in a paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, in April, 1900.

Mr. Herting, who appears to prefer to obtain his chemical information from German sources, bases his criticisms on a translated abbreviated abstract of a reprint in the *CHEMICAL NEWS*, and has apparently not considered it worth while to consult the original article before criticising it. His first statement is that, by the solution of an iron in HCl , volatile SiH_4 forms, causing low results; also that "every iron and steel chemist always uses nitric acid, or nitric and sulphuric, in dissolving irons for silicon determinations." If our collection of methods used in the iron and steel works near Pittsburgh had been translated into German, Mr. Herting would probably have known that in the laboratory of the largest iron and steel works in the world—that of Edgar Thomson—99 per cent of all silicon determinations are made by solution in HCl , and that at least one-half the iron and steel chemists who described their methods at our request do not use nitric acid. I would suggest that, before making any more sweeping assertions as to what "every

* From *Proceedings of Engineers' Society of Western Pennsylvania*, xvii., No. 4. Translated from *Zeit. f. Angew. Chemie*, 1901, p. 165.

iron and steel chemist always does," he should obtain some slight knowledge on the subject, either by visiting the laboratories in the western end of his State, where most of the iron and steel is made, or by consulting the above collection of methods in use here. He might also refer to Fresenius, who recommends solution in HCl.

Any chemist who wishes to know whether there is the slightest truth in the statement that silicon is lost by volatilisation with HCl has only to make duplicate determinations by HCl and by HNO_3 . At my request Mr. J. M. Camp, chemist at the Duquesne Steel Works, and Mr. J. A. Mohr, chemist at the Carrie Furnaces, have done this, and both have written me there is no difference in the results.

In regard to the evolution sulphur method, Mr. Herting seems recently to have discovered what has been a matter of common knowledge among the iron and steel chemists of this section for at least ten years—that is, that low results are obtained by the evolution method if the theoretical factor is used. His charitable assumption that I am ignorant of this fact, because his article of 1899 on the subject was not reprinted in the *CHEMICAL NEWS*, would not have been necessary had he taken the pains to refer to my original article, since I there plainly state that when cold acid is used lower results are obtained. (In the abstract this was not mentioned).

Mr. F. H. Williams, in November, 1892, read before this Section a paper in which he gave results showing that by the use of hot acid higher results are obtained by evolution than when cold acid is used, although these results are still a trifle below aqua regia method results. Mr. S. A. Ford, in whose laboratory I was then employed, stated during the discussion of the paper that he had known for years that part of the sulphur was evolved in a form which was not absorbed.

Dr. F. C. Phillips, who took part in the discussion, was incited thereby to investigate the question thoroughly, and published his results in November, 1895, in the *American Chemical Journal*. The classical work of Campredon and Shulte, in 1897, merely confirmed Dr. Phillips's results. In view of these facts it may well be doubted whether our knowledge on the subject would have been materially increased, even if the *CHEMICAL NEWS* had reprinted Mr. Herting's belated article based on Campredon and Shulte's classical work.

In spite, however, of the above mentioned facts, it is still customary, in the vast majority of iron and steel laboratories, to make nearly all sulphur determinations by evolution, minimising the error, as far as possible, by standardising the iodine solution against a similar iron or steel of known sulphur contents. Thus, at the Edgar Thomson Steel Works laboratory, different factors are used for the same iodine solution, according to whether the sample is a chilled iron or a pig-iron or steel.

Mr. Herting's next objection is to the separation of silica from tungstic acid by volatilisation with HFl. As far as I have been able to determine, his assumption of the formation of a volatile silico-tungstic acid is purely imaginary. Arnold, in his "Steel Works Analysis," p. 136, says:—"The alleged liability of WO_3 to volatilise with silicon unless H_2SO_4 is present has no foundation in fact." I have treated weighed quantities of ignited silica and tungstic acid with HFl, and in no case have found a loss of tungstic acid. At my request Dr. K. F. Stahl, of the General Chemical Company, J. M. Camp, and J. A. Mohr, have investigated the matter, and all have written me there is no evidence of loss of tungstic acid on their repeating the tests.

Mr. Herting next describes his method of determining tungsten in a ferro-tungsten, which appears to be his idea of fulfilling the promise he makes in the beginning of his paper to describe the methods by which correct results can be obtained in the complete analysis of alloy steels. Of this method I will only say, life is short. It involves five evaporations, two fusions, five filtrations, one extraction, and determines tungsten.

He next complains that he has never been able to dissolve chrome alloys in acids. Can it be he has been attempting to analyse a ferro-chrome by the methods I described for chrome steels? I have dissolved many thousand samples of chrome steels in acid, and have yet to find one in which residue was not completely volatile with HFl. Perhaps Mr. Herting will explain this by assuming a volatile compound of silico-chrome with HFl?

Mr. Herting's parting remark is that the method for chromium was fully described by Ledebur, in 1895, in his "Leitfaden für Eisenhüttenlaboratorien," p. 36. Here, again, Mr. Herting would have been spared the necessity of making this unjust accusation if he had carefully read my article in full, as he would have found I titrated chromium in a nitric acid solution after oxidation to chromic acid by potassium chlorate, an entirely different method from that described by Ledebur.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 67).

WE now make mention of another series of experiments, in which the ratio of nitric acid to water was kept constant, whilst the amount of sulphuric acid varied. Thus the results are only to be referred to the action of the sulphuric acid, which may be traced to two causes;—First, to the absolute influence of the sulphuric acid, and afterwards also to the diminution of the percentage of water, owing to its abstraction by the sulphuric acid. These two actions unite in producing their effect, but the greater part must be ascribed to the indirect, according to the results of the last section.

The nitric acid used had the specific gravity 1.40; the ratio $\text{HNO}_3 : \text{H}_2\text{O}$ was found to be after analysis = 184 : 100. Equal weights of this acid were now treated with varying quantities of concentrated sulphuric acid, but care had to be taken to supply water to the nitration mixture with this sulphuric acid, which was 94.91 per cent. This was compensated for by a calculated addition of nitric acid of specific gravity 1.50, so that the ratio $\text{HNO}_3 : \text{H}_2\text{O}$ was constant throughout, and the results of this nitration mixture give us a representation of the action of the sulphuric acid.

The experiments were conducted at the temperature of the room, and the time of nitration lasted twenty-four hours. In this way, nitration up to a proportion of about 33 per cent sulphuric acid was not complete; unchanged cellulose always remained. At first this seemed to us to be no drawback to the experiment. By determination of the nitrogen of the mixture, and from the determination of the unchanged cellulose with sodium methylate, the nitrogen percentage of the nitro-product should be obtained indirectly; in this way we hoped to obtain the lowest stage of nitration, and eventually to find in connection with it the smallest value for the molecular weight of cellulose.

But the cellulose determinations proved to be inexact; determinations from the same product varied between 5 to 10 per cent. These differences are due to the presence of oxycellulose; for, by the influence of the dilute acids, the cellulose is completely or partially converted into oxycellulose. Part of the unchanged cellulose must be dissolved by the slightly alkaline sodium methylate solution, and, in consequence, the determinations of the cellulose appear too low.

In order to obtain a more exact conclusion as to the oxidising action in the nitration mixture, an attempt was

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

made to trace quantitatively the formation of oxycellulose in different nitration mixtures, by a determination of the affinity for basic colour stuffs. Formerly 0.5 grm. of the substance was warmed on the water-bath for an hour with 150 c.c. of a 5 per cent methyl-blue solution in a beaker covered with a watch-glass, after cooling 100 c.c. was poured off, and the loss of methyl-blue determined in the colorimeter of Lummer and Brodhun by comparison with 100 c.c. of standard solution. In the case of a large proportion of oxycellulose, this would have to be diluted from 0.25 to 1.125 per cent.

One grm. pure cellulose fixed 0.0012 grm. methyl-blue. The products of the experiments of Table III. gave the following results.—

TABLE X.

Experiment.						Methyl-blue fixed by 1 grm. substance.
						Grm.
1.	..	..	..	..	..	0.0010
2.	..	..	..	..	..	0.0009
3.	..	..	..	..	..	0.0011
6.	..	..	..	..	..	0.0021
8.	..	..	..	..	..	0.0036
II.	..	..	..	..	..	0.0120

According to these experiments, no formation of oxycellulose would occur in nitration with concentrated acid mixtures, as the products obtained in comparison with cellulose show no increased affinity for methyl-blue. The latter is therefore not changed by introducing NO₂ groups into the cellulose molecule; accordingly the increase of this capacity in using dilute acid mixtures is entirely due to secondary action in the mixture, viz., to the formation of oxycellulose.

A similar phenomenon was observed in the products of the last-named series of experiments. By increasing addition of sulphuric acid to nitric acid 1.4, the affinity of the resulting products for methyl-blue is increased; it reaches a maximum (fixing by 0.0123 grm.) in a nitration mixture with 26 per cent water, and then diminishes again on further concentration of the nitration mixture by addition of sulphuric acid.

The products obtainable with dilute acid mixtures are therefore to be regarded as nitro-oxycelluloses, i.e., mixtures of nitrocelluloses with nitro-oxycelluloses.

This has recently been demonstrated from another direction. According to Dr. Brönnert, and also Leo Vignon, a formation of oxycellulose should also take place in concentrated acid mixtures, which is a contradiction of our experiments. Vignon determined the reducing power of his products against Fehling's solution, and found it approximately equally great with nitrated cellulose as with nitrated oxycellulose. Hence the reducing action does not run parallel with the affinity for basic colour stuffs, and it is therefore scarcely probable that these two phenomena are both due to the same cause—the presence of oxycellulose. By treating our own products, given in Table X., with Schiff's reagent (a fuchsin solution rendered colourless with sulphuric acid) it is seen that the intensity of the red colouration, which is due to the presence of aldehyde groups, increased in a similar manner as the affinity for methyl-blue. These merely qualitative experiments indicate that the formation of aldehyde groups in concentrated acid mixtures is very slight, but that it increases with the dilution of the nitration acids, like the methyl-blue reaction.

If, now, the reducing power of the products depended entirely on the presence of aldehyde groups, it should vary in different nitration mixtures in the same manner as the above reactions. But as Vignon has found no difference, the reducing power cannot stand in a direct relation to the aldehyde groups, i.e., to the oxycellulose. We must therefore adhere to our conclusion that, in using concentrated acid mixtures, there is practically no formation of oxycellulose.

(To be continued).

AN IMPROVED METHOD OF PRODUCING ULTRA-VIOLET-SENSITIVE PLATES.*

By V. SCHUMANN.

(Concluded from p. 68).

The Original and the Improved Method.—My method published in 1893 consisted in diluting with much water an emulsion poor in gelatin, and pouring it into basins in which the silver haloid was deposited from a thick layer upon glass plates laid inside. After the formation of the sensitive film, for which several hours were required, the emulsion was poured off, and the plates dried horizontally.

From this it is obvious that the two methods, the old and the improved, are very similar, but it would be a mistake to judge thus of the photographic nature of their plates; for the two have no more in common than their sensitiveness to ultra-violet rays, the rapid fixing and drying, and their behaviour towards potassium iodide in the developer. In their remaining characteristics they differ widely from each other.

The most striking is their relation to silver iodide. While the emulsion of the older process could stand a considerable quantity of silver iodide, the improved plate becomes fogged in its presence to the extent of being quite useless. All efforts to introduce silver iodide into the sensitive film are frustrated by the easy reduction and excessive intensity which it imparts. I have, nevertheless, after many vain attempts, made it yield to a standing development of seven hours' duration, and obtained negatives tolerably free from fogging, but it is clear that so lengthy a developing process is of no service to spectroscopy.

The improved method depends far more upon the character of the gelatin than does the older. A certain kind of gelatin, used formerly with success, now led to a series of strange irregularities. Besides a variety of spots, the film thus prepared exhibited in the wet condition, a few minutes after pouring off the emulsion, a number of cracks, about 2½ c.m. long, shaped like the tail of a comet, which made the plate useless. In another case one of our best German emulsion-gelatins gave such feebly sensitive films that it was not even possible to reproduce the wave-length 185 μμ, which may be easily done even with the ordinary gelatin plate. But the plate completely changed its character after remaining ten minutes in a bath of warm water (38° C.), thus attaining to a surprisingly high degree of sensitiveness towards ultra-violet rays. In this case the water plays the part of a physical sensitising agent. Its sensitising action depends upon setting free the upper part of the sensitive film from its light-absorbing outer layer, and also increasing the reducing capacity of the silver bromide by warming. The sensitising action of this water-bath upon this kind of plate exceeds every experience that I have had in my years of working with ultra-violet sensitive preparations. Unfortunately the bath causes spots and drying zones of varying sensibility, so that plates of this kind cannot be recommended, all the less so that the sensitising in the bath imperils the stability of the plate.

Of the different kinds of gelatin that I have tried, one only gave permanently good films—that is the soft gelatin already mentioned of English origin that comes into the market under the trade mark Nelson No. 1., known in photographic circles. Therefore I should like to advise all who wish to prepare these plates to use this gelatin and no other.

The older plate was treated with weak developer, the improved plate, on the other hand, may be treated with a solution of unusual strength, more especially not long after preparation of the plate. But, before all things, it is more reliable and more uniformly sensitive, becoming so

in the process in which the coarser silver bromide particles are removed from the film during deposition.

The capacity for decomposition of rays of the sensitive plate makes it highly advantageous to the reproductions of dense groups of lines of large energy differences. My older attempts leave something to be desired in this direction, for in them the lines frequently spread themselves into an indissoluble surface, in which only the most marked lines could be distinguished. This objection, which is entirely due to a lack of half-tones, is obviated in the improved method by the delicate gradation of its negative.

I have already alluded to the action of potassium iodide in the developer of ultra-violet plates. I found that a few drops of a solution of 1:100 accelerated the appearance of the image, but also easily induced fogging, which, in distinction to the fogging of other plates, did not appear simultaneously over the whole film, but spread slowly from the edges to the middle. I have now attempted to utilise this accelerating action of potassium iodide for the improved plate, by immersing it before exposure for a few minutes in dilute solutions of potassium iodide, and then allowing it to dry. The result did not answer my expectation, for the former objections were again apparent.

Use of the Improved Plate in Spectroscopy.—The ultra-violet plate excels all others in giving faithful reproductions of the whole photographic energy of the source of light, from blue to the shortest wave-lengths, while the gelatin dry plate takes the precedence whenever the region lying beyond $220\text{ }\mu$ is not to be taken into consideration.

The sensitiveness of the ultra-violet plate first becomes marked at $220\text{ }\mu$, and increases with the refrangibility of the rays to a high degree.

The gelatin dry plate fails at $182\text{ }\mu$. It is still slightly sensitive towards the shorter waves, but it gives unreliable spectra of these, because in every case, owing to the absorption action of the gelatin, it develops as a white continuous band, and does not give the energy difference of the different waves. Hence, the ultra-violet plate is alone suitable to the photography of the spectrum beyond $182\text{ }\mu$.

THE DETERMINATION OF PHOSPHATES IN POTABLE WATERS.*

By A. G. WOODMAN and L. L. CAYVAN.

(Concluded from p. 71).

The Effect of Silica.

THE properties of dilute solutions of ammonium silicomolybdate were also studied, since silica is the principal substance which interferes with the phosphate test.

Solutions made up with varying quantities of the standard silica solution gave a colour immediately upon adding the reagents. With small and medium amounts of silica the colour was slight compared with that developed in an hour; with high silica standards considerable colour developed instantly. It is interesting to note that ammonium molybdate alone with a silica solution made exactly neutral, develops a faint colour in an hour, but with a phosphate standard no colour appears except in the presence of nitric acid. In twenty-four hours the colour due to the silico-molybdate fades appreciably; it is greener than the colour of the phosphomolybdate.

To determine the time necessary for silica standards to attain their maximum colour, varying standards were mixed with the reagents and 50 c.c. of water and compared at definite intervals with fresh phosphate standards. The readings in terms of the standard phosphate solution are given in the following table:—

C.c. SiO ₂ used.	$\frac{1}{2}$ hour.	1 hour.	1'5 hours.	2'5 hours.	3 hours.	3'5 hours.
0'1	0'03	0'07	0'09	0'03	0'02	0'03
0'7	0'56	0'65	0'67	0'72	0'70	0'67
1'0	0'92	0'96	1'01	1'02	1'07	1'05
3'0	2'75	2'88	2'95	3'01	2'95	2'95
7'0	6'65	6'75	6'95	7'00	7'10	7'20
10'0	9'70	9'95	9'99	9'95	9'95	—

C.c. SiO ₂ used.	$\frac{1}{2}$ hours.	5 hours.	5'5 hours.	6 hours.	6'5 hours.	7 hours.
0'1	0'02	0'01	0'01	0'01	0'008	0'008
0'7	0'67	0'67	0'66	0'66	0'65	0'65
1'0	1'05	1'04	1'03	1'03	1'02	1'02
3'0	3'10	3'20	3'20	3'25	3'30	3'40
7'0	7'20	7'20	7'25	7'25	7'30	7'35
10'0	9'95	9'95	9'95	9'95	9'95	9'90

It will be noticed that the lower standards reach a maximum in about two or three hours, and then begin to fade; the medium standards do not seem to reach a maximum even after seven hours.

A number of silica standards, after standing one hour, were heated from 20° to 100° in a water-bath. The colour did not change in intensity until 70° — 80° was reached, when it began to fade, decreasing up to 100° . The colour did not return to its original intensity on cooling slowly to 20° .

Experiments made to determine the conditions under which minute quantities of silica might be rendered entirely insoluble showed that evaporation with nitric acid and heating at 100° for an hour was insufficient; when the same standards were evaporated and heated at 135° for an hour, re-combination took place and some of the silica remained soluble. On heating the residues for two hours at 100° instead of one hour, however, no silica remained soluble. The results are shown in the following table. 1, 2, and 5 c.c. of the standard silica solution were diluted to 50 c.c., 10 drops of nitric acid were added, the solutions evaporated to dryness in porcelain dishes, and heated at different temperatures for two hours. The residue was taken up in cold water and the colour read after standing one hour:—

Temperature.	Readings.			Per cent undehydrated SiO ₂ .		
	1 c.c.	2 c.c.	5 c.c.	1 c.c.	2 c.c.	5 c.c.
60°	0'5	1'2	2'0	50	60	40
80°	0'3	0'7	0'9	30	35	18
100°	0'0	0'0	0'0	00	00	00
135°	0'1	0'4	1'0	10	20	20
150°	0'4	0'5	1'1	40	25	22
190°	0'6	0'8	1'1	60	40	22

Other Compounds which might Interfere.

Since vanadium and titanium resemble phosphorus and silicon quite closely in many of their properties, vanadates and titanates might interfere with the determination of phosphates by a colorimetric method. Titanium is especially liable to occur in the natural waters of regions containing diorites and titanium-bearing ores like ilmenite. The presence of these elements has been observed in natural waters.

Dilute solutions of sodium titanate gave a pale greenish yellow colour with ammonium molybdate and nitric acid, but much less intense than the phosphate colour. The colour did not fade within an hour, but at 20° C. it took twelve minutes for it to appear. By evaporation with nitric acid, and subsequent heating at 100° for two hours, the titanium oxide was rendered completely insoluble.

Ammonium vanadate gave with the ammonium molybdate alone a yellow colour which was permanent for several hours, but upon the addition of nitric acid this colour faded completely in five minutes. Experiments with a standard solution of ammonium vanadate showed that the colour given by as much as 0'0003 grm. of V_2O_5 in 50 c.c. of water fades out entirely in four minutes. Incidentally it was found that 0'000001 grm. of V_2O_5

* Contributions from the Laboratories of the Massachusetts Institute of Technology. From the *Journal of the American Chemical Society*, xxi., No. 2.

could be detected readily in a volume of 50 c.c. It is evident that the small quantities of vanadium which occur in natural waters will not interfere with the determination of phosphates.

Colorimetric Estimation of Phosphates in the presence of Silica.

The previous results had shown the possibility of a method based on the dehydration and elimination of the silica. The conditions must be such that the total phosphate or a definite portion of it shall be left intact and that the silica shall be rendered entirely insoluble. The following method was finally adopted as the one giving the most satisfactory results:—

Fifty c.c. of the water and 3 c.c. of nitric acid (sp. gr. 1.07) are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 c.c. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four c.c. of ammonium molybdate and 2 c.c. of nitric acid are added, the contents of the tube mixed, and the colour compared after three minutes with standards made by diluting varying quantities of the standard phosphate solution to 50 c.c. and adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as just described will be sufficient for ordinary work. If a more exact determination of the phosphate is required, a slight correction should be applied in each case. These corrections were determined by making a number of determinations by the method. The results are shown in the following table. The first two series had two c.c. of standard silica solution added to each test; the others had only the phosphate:—

Phosphate added.	Phosphate found.						Average.	Correc- tion.
0.1	0.07	0.09	0.10	0.10	0.09	0.09	0.09	0.01
0.5	0.46	0.47	0.46	0.45	0.43	0.45	0.45	0.05
0.7	0.63	0.64	0.64	0.65	0.64	0.66	0.65	0.05
1.0	0.85	0.85	0.86	0.86	0.84	0.83	0.85	0.15
3.0	2.55	2.65	2.50	2.50	2.60	3.65	2.60	0.40
5.0	4.55	4.55	4.45	4.45	4.50	4.50	4.50	0.50
7.0	6.65	6.60	6.55	6.55	6.60	6.65	6.60	0.40
10.0	9.60	9.65	9.55	9.60	9.60	9.55	9.60	0.40

Since organic life is present in greater numbers and is more active in surface waters than in ground waters it is evident that the determination will be of greatest value for the examination of wells. Well-waters are usually colourless, and to them the method may be applied directly. It is not yet suitable for coloured waters. The determination of phosphates is at present being carried on in this laboratory as a routine determination, and the results will be published as soon as sufficient data have accumulated to render a discussion of the entire question of value.

COMPOUNDS OF METHYL SULPHIDE WITH
HALIDES OF METALS.*

By FRANCIS C. PHILLIPS.

(Concluded from p. 69).

Compound of Methyl Sulphide with Cuprous Chloride.

WHEN methyl sulphide is added to a concentrated solution of cupric chloride, the colour of the liquid changes from green to dark brown, and heat is evolved. After standing for a few hours, a mass of white crystalline scales forms at the bottom. The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green

during drying. Exclusion of air does not serve completely to prevent this change of colour. The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound. Boiling with water seems to expel part of the methyl sulphide. The substance dissolves in ammonia and in nitric acid.

Caustic alkalis decompose it, yielding an insoluble brownish red powder. Digestion of the substance with hydrogen sulphide gradually changes it to copper sulphide. This reaction was made use of for a determination of the copper, the sulphide being ignited, re-dissolved, precipitated by sodium hydroxide, and weighed as cupric oxide. Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned. As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralisation by zinc, and titration by silver nitrate solution. Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride. Sulphur was determined by the method of combustion in oxygen already described. The results of analysis were as follows:—

	Per cent.
Copper	39.12
	39.13
Chlorine	21.85
	21.80
	21.76
	21.77
	21.76
	21.60
Sulphur	19.62
	19.70

The calculated percentages of the constituents named in the case of a compound having the composition $\text{CuCl}(\text{CH}_3)_2\text{S}$ are:—

	Per cent.
Copper	39.46
Chlorine	22.00
Sulphur	19.90

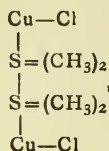
Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100° C., and continues to lose methyl sulphide until the temperature reaches about 200° C. After heating to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21.53 per cent of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $\text{CuCl}(\text{CH}_3)_2\text{S}$, is characterised by great intensity, as evidenced by the heat evolved and by the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated, and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white colour and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to be the case in cuprous chloride,



The constitution of the compound might perhaps be expressed by the formula,

* Journal of the American Chemical Society, vol. xxiii., No. 4.



in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend merely on whether there are one or two carbon atoms linked to the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character, as if the chlorine atom alone were present.

Compound of Methyl Sulphide with Gold Chloride.

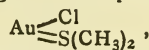
When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs, while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas-light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colourless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced, and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained:—

	Per cent.
Gold	67.16
	66.98
	66.77
	67.42
Chlorine	12.32
	12.35
	11.97
	11.74
Sulphur	10.99
	10.88

These results suggest the composition—



since calculation shows that such a compound would contain:—

	Per cent.
Gold	66.90
Chlorine	12.02
Sulphur	10.87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100°, and continues until the temperature approaches 200°. At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen

than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating, and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover, in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

Condition in which Carbonic Acid exists in Natural Waters.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water, and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of these bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds CaCO_3 and MgCO_3 , the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such salts have never been isolated. These salts are presumed to have the composition represented by the formulæ $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$, respectively.

The gas carbon dioxide (CO_2) is quite soluble in water, and therefore may exist in natural waters in amounts greater than is required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula H_2CO_3 .

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If the carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid"; if it is combined indirectly with the base as in the form of the bicarbonates, it is termed "half-bound carbonic acid"; and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total

* *Journal of the American Chemical Society*, xxiii., No. 6.

carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid," or both, is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover, ground waters which become exposed to the air lose the larger proportion of their free carbonic acid, and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory might contain from six to ten parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present, and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water	0	0
After twenty-four hours ..	2.2	2.2
After forty-eight hours ..	15.0	13.2
After seventy-two hours ..	0.9	0.9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory, and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate (CaCO_3) is thereby precipitated, and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), when exposed to the air of the laboratory:—

	A. Carbonic acid in solution. Parts per million.			B. Carbonic acid in solution. Parts per million.		
	Free.	Half-bound.	Fixed.	Free.	Half-bound.	Fixed.
Original water	52.8	109.4	109.4	52.8	109.4	109.4
After 24 hours	7.9	—	—	7.0	—	—
After 48 hours	1.3	—	—	1.1	—	—
After 72 hours	0	80.7	84.5	0	80.7	84.5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate (MgCO_3) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free and 12 per cent of its half-bound carbonic acid in less than three days when exposed to the air of the laboratory. This solution, therefore, contained 12 per cent of its total magnesium carbonate in the form of normal magnesium carbonate (MgCO_3). On the other hand, the calcium bicarbonate solution, as shown above, contains only 4 per cent of its total calcium carbonate in

the form of the normal carbonate (CaCO_3). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However, solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid, or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (i.e., contain free carbonic acid), but the acidity is always very slight, and the state of equilibrium seems to be reached when the lime is all in the form of the bicarbonate. On the contrary, weak solutions of magnesium carbonate, while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of these two compounds. That these facts have a bearing on certain classes of natural waters will be shown later.

Principles on which Methods for the Estimation of Carbonic Acid are Based, with a Discussion of the Errors Affecting their Accuracy.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and also to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer (*N. Rep. Pharm.*, x., i.). Trillich (*Ztschr. Angew. Chem.*, June 15, 1889, p. 337) modified this method in order to avoid certain difficulties arising in the original method, and as this modification is quite radical, the process as carried out by him can be considered practically as a new method. Seyler (*CHEM. NEWS*, lxx., 1894, 104; and *Analyst*, 1897, xxii., 312), advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

(To be continued).

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 66).

Specific Gravity of the Zomba Enstatite.

29. SINCE the proportions by weight of the three constituents of the undecomposed material and the specific gravities of two of them (felspar and chromite) are known, it is now possible from the specific gravity of the mixture (§ 14) to calculate the specific gravity of the third constituent (enstatite). The specific gravity of oligoclase, Ab_3An_1 , is 2.66; that of chromite varies from 4.32 to 4.57 (Dana), the mean of which is 4.44; that of the mixture was found to be 3.171 (§ 14). The total volume of a mixture being the sum of the volumes of the constituents, it follows that, if x be the specific gravity of the enstatite,—

$$\frac{78.71}{x} + \frac{19.84}{2.66} + \frac{1.45}{4.44} = \frac{100}{3.171}.$$

Whence x is 3.314.

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

The specific gravity of the Lodran enstatite was directly determined by Professor Tschermak to be 3.313.

Undecomposed Material: Amount of Action of Hydrochloric Acid and Sodic Solution.

30. The trace of undecomposed material, which, after treatment with hydrofluoric and sulphuric acids, weighed 0.0014 (§ 17), must before that treatment have weighed 0.0017 (§ 19); hence SiO_2 is 0.0746; and the total amount of undecomposed silicate is $0.0017 + 0.8807 + 0.0363$ or 0.9187; for ignition does not appreciably alter the weight of the undecomposed material (§ 18). After deduction of SiO_2 0.0049 due to the sodic solution itself (§ 13), we have, for the SiO_2 due to the silicate, 0.0697.

For the hydrochloric acid extract:—

$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0150 consisted of Fe_2O_3 0.0140 (corresponding to FeO 0.0127), Al_2O_3 0.0009, SiO_2 nil.

Deducting 0.0054 from $\text{Mg}_2\text{P}_2\text{O}_7$ 0.0649 as being really $\text{Ca}_2\text{P}_2\text{O}_7$ due to the action of the nitric acid on the porcelain (§ 20), we have $\text{Mg}_2\text{P}_2\text{O}_7$ 0.0595, corresponding to MgO 0.0215. Collecting the results:—

	Acid extract.	Sodic extract.	Total extract.
SiO_2	—	0.0697	0.0697
FeO	0.0127	—	0.0127
MnO	—	—	—
MgO	0.0215	—	0.0215
CaO	0.0076	0.0023	0.0099
Al_2O_3	0.0009	0.0062	0.0071
K_2O	Undet.	Undet.	Undet.
Na_2O			
Total extract			0.1209
Undecomposed residue			0.9187
Weight found			1.0396
Weight taken			1.0388

Hence it follows that when the undecomposed material is subjected to the action of hydrochloric acid and sodic solution in the same way and for the same length of time as in the analysis of the mixed powder itself, no less than 11.64 per cent pass into the acid or sodic solution. As there is little alumina in the acid extract, either the felspar is only very slightly attacked by the acid, or the alumina is set free in such a form as to be only with difficulty soluble in the acid, though removable by the sodic solution (*Fourn. Chem. Soc.*, 1882, vol. xli.; *Transactions*, p. 159); more probably the greater part of the decomposition of the felspar is due to the sodic solution itself.

If we allow soda in sufficient proportion to form oligoclase with the alumina (§ 24) the percentage composition of the total extract is—

SiO_2	56.44
FeO	10.29
MnO	—
MgO	17.41
CaO	8.02
Al_2O_3	5.75
K_2O	2.09
Na_2O	
	100.00

The total extract has thus nearly the same composition as the original mixture (§ 23). The chief part of the solvent action on the enstatite is due to the acid; the silica set free by this action is removed by the sodic solution, which at the same time acts to some extent on the felspar, taking all the constituents into solution, and probably to some extent on the enstatite, removing the silica and lime but leaving its oxide of iron and magnesia in the final residue. The corresponding oxide of iron and magnesia left in the undecomposed residue by the action of the previous sodic solution will have passed into the acid extract.

Unattracted Material: Treatment with Mercuric Solution.

31. Fe_2O_3 0.0021 (§ 9) corresponds to Fe 0.0015. Hence the total amount of alloy extracted by the mercuric solution from 4.9856 grms. of the unattracted material was at most 0.0022, containing 31.82 per cent of nickel; as already stated, the high percentage of the nickel was already manifested by the colour of the extract. This again points to the easy oxidation of the iron of the finer particles of nickel-iron during the exposure to the air in the course of the magnetic separation and afterwards; the nickel being less easily oxidised and less readily attracted by the magnet, the percentage of the nickel in the metallic portion still left with the unattracted material will be higher than in the original nickel-iron.

Unattracted Material: Alkalis.

32. K_2PtCl_6 0.0040 (§ 8) corresponds to KCl 0.0012; 0.0036, adherent to the filter and ignited, if taken as Pt_2KCl , corresponds to KCl 0.0016; making altogether KCl 0.0028.

From the blank experiment (§ 22) the KCl due to the reagents is 0.0021; hence only KCl 0.0007 can be assigned to the silicate.

The mixed chlorides due to the silicate weigh 0.0135 (§ 8)—0.0021 (§ 22), or 0.0114; the NaCl is thus 0.0107.

These amounts of NaCl and KCl correspond respectively to Na_2O 0.0057 and K_2O 0.0004 for 0.4815 of material, and to Na_2O 1.18 and K_2O 0.08 per cent.

As the total amount of matter extracted from the unattracted material by boiling water amounted to only 0.26 per cent, and part of it consisted of calcium and magnesium, it is inferred that the alkalis were present in the unattracted material as constituents of an insoluble compound, presumably felspar.

Unattracted Material: First Portion.

33. The trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids weighed 0.0039 (§ 10), must before that treatment have weighed 0.0047 (§ 19); and the total amount of undecomposed material is $0.0047 + 0.9186 + 0.1328$ or 1.0561, for ignition does not appreciably alter the weight of undecomposed material (§ 18).

The true SiO_2 is 0.4909—0.0047 or 0.4862; but of this 0.0049 are due to the sodic solution itself (§ 13); the SiO_2 really due to the silicate is thus 0.4813. Of the $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0048, the Fe_2O_3 was small, and probably only that from the sodic solution itself, 0.0009 (§ 13); the SiO_2 was 0.0031 (making the total SiO_2 0.4844) and (by deficit) Al_2O_3 is 0.0008.

The $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.4639 from the acid extract consists of Fe_2O_3 0.4578 (corresponding to FeO 0.4120), Al_2O_3 0.0040 (and SiO_2 0.0021 due to the action on the vessels).

Further, 2.5065 of unattracted material contains an amount of sulphur (§ 7) corresponding to FeS (troilite) 0.1412, which is itself equivalent to FeO 0.1155; as this iron is in the acid extract, only FeO 0.2965 (i.e., 0.4120—0.1155) is due to the silicate.

MnS 0.0068 corresponds to MnO 0.0055.

(NiO 0.0001 may be neglected in the calculations).

Hence we have—

		Percentages.
Undecomposed material	1.0561	42.13
Troilite	0.1412	5.63
SiO_2	0.4844	19.33
FeO	0.2965	11.83
MnO	0.0055	0.22
MgO	Undet.	Undet.
CaO	Undet.	Undet.
Al_2O_3 { Acid extract 0.0040 Sodic extract 0.0008 }	0.0048	0.19
K_2O	Undet.	Undet.
Na_2O	Undet.	Undet.
Total	1.9885	79.33
Weight taken	2.5065	100.00

Unattracted Material: Second Portion.

34. The amount of volatile material corresponding to 2.7333 of the material taken for analysis would be 0.0680 (§ 11), and the weight of the pure material was thus 2.6653.

The trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids, weighed 0.0017 (§ 11), must, before that treatment, have weighed 0.0021 (§ 19); and the total amount of undecomposed material is 0.0021 + 1.0981 + 0.0516, or 1.1518, for the weight of the undecomposed material is not appreciably altered by the ignition (§ 18).

The true SiO_2 is thus 0.5296 - 0.0021 or 0.5275; but of this, 0.0049 is due to the sodic solution itself (§ 13); the SiO_2 really due to the silicate being therefore 0.5226.

The $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.0065 consists of Fe_2O_3 0.0020, Al_2O_3 0.0035, and SiO_2 0.0010 (making the total SiO_2 0.5236); deducting Fe_2O_3 0.0009 as due to the sodic solution itself, Fe_2O_3 0.0011 has passed into the sodic solution from the silicate (possibly through finely-divided silicate passing through the pores of the filter).

The $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2$ 0.5013 of the acid extract consists of Fe_2O_3 0.4960, Al_2O_3 0.0019, and SiO_2 0.0034 (due to action on the vessels).

(NiS ignited 0.0012 may be omitted in the calculations).

MnS 0.0074 corresponds to MnO 0.0060.

The $\text{Mg}_2\text{P}_2\text{O}_7$ (pure) is 1.3834 (§ 11) - 0.0054 (§ 20) or 1.3780, corresponding to MgO 0.4989.

The total Fe_2O_3 is 0.4960 + 0.0011 or 0.4971, corresponding to FeO 0.4474; further, 2.6653 of the unattracted material contain an amount of sulphur (§ 7) corresponding to FeS (troilite) 0.1502, which itself is equivalent to FeO 0.1259; as this iron is in the acid extract, only 0.3215 (i.e., 0.4474 - 0.1259) of FeO is due to the silicate.

The total CaO obtained is 0.0013 + 0.0105 or 0.0118; from this must be deducted 0.0005 as due to the sodic solution (§ 13).

Also 2.6653 of the unattracted material contains (§ 22) K_2O 0.0022, Na_2O 0.0315; and the 1.1518 of undecomposed material contain (§ 22) K_2O 0.0021, Na_2O 0.0182; hence there must have passed into the acid and alkaline solutions K_2O 0.0001 (or nil) and Na_2O 0.0133.

Collecting the results we have:—

		Percentages.
Undecomposed material	1.1518	43.21
Troilite	0.1502	5.64
SiO_2	0.5236	19.65
FeO	0.3215	12.06
MnO	0.0060	0.23
MgO	0.4989	18.72
CaO	0.0113	0.42
Al_2O_3 { Acid extract 0.0019 Sodic extract 0.0035 }	0.0054	0.20
K_2O	Nil	Nil
Na_2O	0.0133	0.50
Total	2.6820	100.63
Weight taken	2.6653	100.00

(To be continued).

ON NITROMETER WORK.

By C. H. SHEPARD.

THE following work was done on the usual nitrometer, composed of a decomposing bulb and reservoir, and the complement of a measuring tube, reduction tube, and reservoir. The measuring tube had a capacity of 140 c.c. The potassium nitrate used was Merck's, chemically pure, re-crystallised. About 0.5 grm. was used for each determination. The temperature of the laboratory, while the work was being done, was approximately 68° F. The dry potassium nitrate was weighed out into tared weighing-bottles, and about 15 c.c. of sulphuric acid added. The bottles were then stoppered and set aside for about eighteen hours, or over night, by which time a clear solution was obtained if the acid used was over 90 per cent

H_2SO_4 , but if of less strength a residue, presumably of potassium sulphate, was left. The contents of the weighing-bottles were transferred to the decomposing bulb with the aid of a wash-bottle containing acid of the same strength as that used in the weighing-bottles. In each determination 32 c.c. of acid were used. The strengths of sulphuric acid used and the volume in cubic centimetres of nitric oxide (NO) per grm. of potassium nitrate for each acid are as follows:—

Strength of sulphuric acid in per cent.	C.c. of nitric oxide per grm. potassium nitrate.					
	I.	II.	III.	IV.	V.	Average.
98.03	222.0	221.8	222.0	222.3	222.3	222.08
96.92	223.2	223.0	223.3	223.3	—	223.2
96.92	224.0	224.3	224.4	224.4	224.4	224.3
95.14	225.1	224.8	225.0	225.2	225.0	225.0
94.07	225.0	225.0	224.9	225.2	225.0	225.02
93.05	225.1	225.0	224.8	224.9	225.0	224.96
90.90	225.0	224.9	224.9	225.0	225.0	224.96
85.04	225.3	225.1	225.3	225.0	225.3	225.2
80.14	226.2	226.0	226.2	226.2	226.0	226.1

A difference of 4.02 c.c. of nitric oxide is thus obtained by the use of the strongest and weakest acids. It seems probable that this is due to the varying absorptive powers for nitric oxide, of the different strengths of sulphuric acid used.

Lunge (*Journ. Soc. Chem. Ind.*, 1885, p. 447) states that "1 c.c. of concentrated vitriol dissolves 0.000593 grm. = 0.035 c.c. NO." If this 4.02 c.c. of nitric oxide per grm., or 2.01 per half grm. of potassium nitrate, is due to the difference of solubility of nitric oxide in the first and last acids used, then 32 c.c. of 98.03 per cent sulphuric acid absorbs 2.01 c.c. nitric oxide, and 1 c.c. absorbs 0.0628 c.c. nitric oxide. For nitrometer work acid of about 95 per cent H_2SO_4 appears to be the best. Weaker acid attacks the mercury more readily, and decomposes nitric acid more slowly. There is no objection to stronger acid except the difficulty of obtaining it. The chemically pure acid made by a well-known company has been found to vary from 95.0 to 98.0 per cent H_2SO_4 .—*Journal American Chemical Society*, xxiii., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

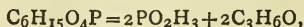
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 4, July 22, 1901.

Experiments with Uranium at Very Low Temperatures.—Henri Becquerel.—The author examines the action of liquid air on uranium, with regard to its radio-activity. The action is measured by means of an extremely delicate electroscope. At the temperature of boiling air the current apparently is reduced to one-half of that obtained by the action of the uranium at a temperature of 24.8°. The author also repeats the experiment already performed by Prof. Dewar of plunging into liquid air, or better into liquid hydrogen, a crystal of uranium nitrate, the latter becoming spontaneously luminous.

The Nature of X Rays.—Jules Semenov.—The author's experiments lead him to the conclusion that X rays represent the directions of transmission, through the medium of ether, of electric vibrations. These vibrations are communicated to all bodies which they meet during their passage. When the bodies are charged with electricity, and when they are protected against discharge by convection, they lose their charge by radiation.

Action of Hypophosphorous Acid on Acetone.—C. Marie.—Crystalline hypophosphorous acid appears to have no action when heated with acetone. However, if the solution is kept boiling for some time the temperature rises

regularly, the liquid at the same time becoming more and more brown coloured and viscous. On cooling, crystals separate out. These have the formula—



and are a monobasic acid. A second body can be obtained from the filtrate. This latter is a bibasic acid characterised by the insolubility of its lead salt. It has the formula $\text{C}_3\text{H}_9\text{O}_4\text{P} = \text{PO}_3\text{H}_3 + \text{C}_3\text{H}_6\text{O}$.

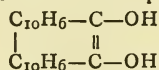
Preparation of Pure Cerium Oxide.—Jean Sterba.—The author modifies MM. Wyruboff and Verneuil's method of preparation of pure cerium. He uses electrolysis as an agent of oxidation, this rendering the operations much more rapid. Cerium oxide when perfectly pure can have a decided colour, but when prepared with elimination of nitrogen it becomes snow white. The action of hydrogen on cerium oxide effects an incomplete reduction and formation of Ce_2O_3 . Zinc also reduces the oxide CeO_2 .

Thermic Examination of the Hydrates of Solid Soda.—M. de Forcrand.—M. Berthelot gives for the heat of solution of NaOH the number +9.78 cal. at 10.5°, whilst for a specimen of pure commercial soda of composition $\text{NaOH} + 0.76\text{H}_2\text{O}$ the number +7.31 cal. is given. Thomsen gives +9.94 cal. as the heat of solution of NaOH at 17.32°. The author re-examines these numbers and uses them to discover a number of solid hydrates:— $3\text{NaOH} + 2\text{H}_2\text{O}$, $\text{NaOH} + \text{H}_2\text{O}$, $2\text{NaOH} + 7\text{H}_2\text{O}$.

Oxidation of Propylglycol by Mycoderma aceti.—André Kling.—The bacteria of sorbose and the *Mycoderma aceti* of Orleans act in the same manner on racemic propylglycol, oxidising the secondary alcoholic function of the left isomer and transforming it into acetol. The author intends to complete this investigation of the parallelism of the action of the two ferments and to extend it to other glycols.

Action of Pyridic Bases on Tetrahalogen Benzoquinones.—Henri Imbert.—The author previously announced that pyridic bases act on chloranile and bromanile, giving substitution bodies of phenolic function, if, however, one of the α -positions of the pyridic radicle is not taken. The pyridine and the tetrachloroquinone, for example, give the derivatives $\text{C}_5\text{H}_4\text{N}=\text{C}_6\text{Cl}_2\text{O}_2-\text{OH}$ or $\text{HO}-\text{C}_5\text{H}_4\text{N}=\text{C}_6\text{Cl}_2\text{O}_2$. These bodies easily lose an atom of chlorine under the influence of alkalis.

The Hydrobromic and Hydrochloric Ethers of the Supposed Bi-naphthylene-glycol.—R. Fosse.—Under the name of aromatic glycol Rousseau described a derivative of binaphthylene which should possess the formula—



This body, obtained as a secondary product during the action of chloroform on β -naphthol, is formed by the splitting off of two molecules of oxynaphthoic aldehyde, $\text{OH}-\text{C}_{10}\text{H}_6-\text{COH}$, which should eliminate their two ox-hydriles and transform their two aldehyde functions into two tertiary alcoholic functions. The author shows by means of his experiments that the hydrochloric and hydrobromic ethers which are derived from binaphthylene glycol are in reality the monobromo and monochloro derivatives of dinaphtho-xanthene.

Action of Gaseous Ammonia on the Chlorohydrates of the Fatty Amines.—Félix Bidet.—The author examines the action between ammonia gas and the chlorohydrates of monoethylamine and diethylamine.

MISCELLANEOUS.

Institute of Chemistry Examinations.—Pass Lists (July, 1901).—*Intermediate Examination*: A. G. Armstrong, Glasgow and W. of Scot. Tech. Coll. and at King's Coll., London; F. W. F. Arnaud, King's Coll.,

London, also under Messrs. W. F. Lowe, and C. H. Cribb, F.F.I.C.; J. W. G. Brooker, Finsbury Tech. Coll., London; H. Finemore, Pharmaceutical Society's Laboratory, and at King's Coll., London; G. F. D. Green, King's Coll., London, and at Central Tech. Coll., London; E. V. Jones, University, Birmingham; T. B. Kirkhope, Glasgow and W. of Scot. Tech. Coll.; W. T. Munro, Glasgow and W. of Scot. Tech. Coll.; H. A. D. Neville, B.Sc. (Lond.); W. H. Peters, Univ. Coll., Nottingham; J. H. Walker, Glasgow and W. of Scot. Tech. Coll.; T. E. Wallis, B.Sc. (Lond.), Pharmaceutical Society's Laboratory; C. J. Wilson, Finsbury Tech. Coll., London. *Examination in General Practical Chemistry for Fellowship*: J. B. Coppock, Univ. Coll., Nottingham, and at Royal Coll. of Science, London. *Final A.I.C. Examination—Branch "A" (Mineral Chemistry)*: B. G. McLellan, Glasgow and W. of Scot. Tech. Coll.; D. Northall-Laurie, King's Coll., London; F. R. O'Shaughnessy, A.R.C.Sc., Royal Coll. of Science, London; P. W. Tainsh, Glasgow and W. of Scot. Tech. Coll.; T. Taylor, Glasgow and W. of Scot. Tech. Coll.; W. Scott Tebb, M.A., M.D. (Cantab.), Cambridge University, and King's Coll., London; F. Wade, A.R.C.Sc., Royal Coll. of Science, London; F. W. Watson, B.Sc. (Lond.), Glasgow and W. of Scot. Tech. Coll. *Branch "B" (Metallurgical Chemistry)*: C. T. Abell, B.Sc. (Vit.), Owens Coll., Manchester; A. W. Comber, Finsbury Tech. Coll. *Branch "D" (Organic Chemistry)*: H. D. Dakin, B.Sc. (Vit.), Yorkshire Coll., Leeds; E. Hinks, King's Coll., London; A. Slaton, B.Sc. (Lond.), University, Birmingham; R. E. B. Smith, B.Sc. (Lond.), University Coll., London. *Branch "E" (Analysis of Food and Drugs and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy)*: B. R. Coysch, King's Coll., London; A. W. Ellis, University, Birmingham, and under J. K. Colwell, Esq., F.I.C.; D. S. Jardin, A.R.C.Sc.I., Royal Coll. of Science, Dublin; T. Macara, Glasgow and W. of Scot. Tech. Coll., and under Dr. J. Clarke, F.I.C.; S. E. Melling, Owens Coll., Manchester, and under A. H. Allen, Esq., F.I.C.; J. Webster, University, Birmingham, and under J. K. Colwell, Esq., F.I.C. *Branch "E" (Analysis of Food and Drugs and of Water)*: J. A. Brown, University Coll., Nottingham. The Examiners in Chemistry were Dr. Bernard Dyer, F.I.C., and Dr. W. Palmer Wynne, F.R.S., F.I.C. The Examiner in Therapeutics, Pharmacology, and Microscopy was Dr. A. P. Luff, F.R.C.P., F.I.C.

OLD PLATINUM

IN ANY FORM PURCHASED FOR CASH.

Highest prices allowed by

ROBERT PRINGLE & SONS, Gold and Silver Refiners, &c., 40 and 42, Clerkenwell Rd., E.C.

Photographic Residues reduced and purchased.



GENUINE WORKING RECIPES,

IN THE

OIL, GREASE, SOAP, PAINT, COLOUR, VARNISH, and ALLIED TRADES.

Latest Up-to-date Processes and Methods—English and Continental Household and Trade Specialities, in every line. (Many Unpatented).

Consultations—Correspondence by Letter.

Analysis—Samples Matched—Identicals Found—Samples and Articles Received for Testing and Analysis—Certificates Given—Contract Work Undertaken.

WRITE FOR FULL LIST, FREE.

E. SCOTT,

Practical Chemist, Analyst, and Expert.

168, Church Street, NORTH SHIELDS.

THE CHEMICAL NEWS

VOL. LXXXIV., No. 2178.

ON THE BEHAVIOUR OF OXY-HÆMOGLOBIN, CARBONIC-OXIDE-HÆMOGLOBIN, METHÆMOGLOBIN, AND CERTAIN OF THEIR DERIVATIVES, IN THE MAGNETIC FIELD, WITH A PRELIMINARY NOTE ON THE ELECTROLYSIS OF THE HÆMOGLOBIN COMPOUNDS.*

By ARTHUR GAMGEE, M.D., F.R.S.,
Emeritus Professor of Physiology in the Owens College,
Victoria University.

1. *The Observations of Faraday and Plücker on the Diamagnetic Properties of the Blood.*

In the course of his investigations on magnetism and diamagnetism, read before the Royal Society in the year 1845, Faraday ("On New Magnetic Actions and on the Magnetic Condition of all Matter," *Phil. Trans.*, 1846, Part I.), found that, notwithstanding the iron which its colouring matter contains, the blood is a diamagnetic liquid. "I was much impressed," he remarked, "by the fact that blood was not magnetic, nor any of the specimens tried of red muscular fibre of beef or mutton. This was the more striking, because, as will be seen hereafter, iron is *always* and in almost all states magnetic. But in respect to this point it may be observed that the ordinary magnetic property of matter and this new property are in their efforts opposed to each other; and that when this property is strong it may overcome a very slight degree of ordinary magnetic force, just as also a certain amount of magnetic property may oppose and effectually hide the presence of this force" (Faraday's "Experimental Researches in Electricity," 1855, vol. iii., p. 36, para. 285). Faraday further found the blood to behave like all the constituent tissues of animal bodies which he investigated, and was led to state that "if a man could be suspended with sufficient delicacy, after the manner of Dufay, and placed in the magnetic field, he would point equatorially; for all the substances of which he is formed, including the blood, possess this property" (Faraday's "Experimental Researches in Electricity," vol. iii., p. 36, 2281).

De la Rive and Brunner,† later, suspending a bound-up frog between the poles of an electro-magnet, observed it to assume an equatorial position, thus realising Faraday's prediction that a complex animal organism must be diamagnetic in accordance with the properties of its constituent tissues and of the water which enters so largely into their composition.

Shortly after the publication of Faraday's researches on diamagnetism, Professor Plücker,‡ of Bonn, in a well known paper, which appeared in 1848, after describing the characteristic behaviour of magnetic and diamagnetic liquids contained in watch-glasses placed upon and between the poles of powerful electro-magnetics, gave the results of his observations on the diamagnetic properties of the blood. He not only confirmed, by experimenting on the blood of the frog, of man, and of the ox, the

accuracy of Faraday's statements, but by employing the microscope in his observations he was able to show that the blood corpuscles are more strongly diamagnetic than the liquid in which they float.*

2. *Objects of the present Investigation.*

At a time when all facts bearing on the physical properties and the chemical relations and structure of the blood-colouring matter are rightly claiming the attention of many of the leading workers in physiological chemistry, it appeared to me very desirable to examine the magnetic properties of the crystalline blood-colouring matter itself, in the condition of utmost available purity, and, whatever the results might be to extend the inquiry to its leading iron-containing derivatives.

Although Faraday had shown that the blood is diamagnetic, and Plücker that the blood corpuscles are more decidedly diamagnetic than the liquid in which they float, it was yet conceivable, though improbable, that the iron-containing hæmoglobin would prove to be a feebly magnetic body, of which the true magnetic behaviour was concealed by the substances with which it is associated in the blood corpuscles. Whether hæmoglobin proved to be magnetic or diamagnetic, it obviously would be of great interest to examine the magnetic properties of the iron-containing substances which the blood-colouring matter yields when it is decomposed by acids in the presence of oxygen, and in the event of a difference between the magnetic behaviour of the mother-substance and its derivatives, to push the inquiry in a direction likely to lead to the discovery of the cause of the discrepancy. In pursuance of such an object I have been led to inquire whether the pure blood-colouring matter in aqueous solution is an electrolyte, and having discovered that it is one, to examine the results of its electrolysis. On this part of my inquiry the statements which I have to make in this paper are strictly preliminary, and, except in the first most interesting particular that oxy-hæmoglobin and CO-hæmoglobin separate in the first instance from their aqueous solutions when these are subjected to very feeble currents, are to be considered as liable to correction by future more extended work.

3. *The Electro-magnet employed in the present Research.*

The electro magnet employed was constructed by Ladd many years ago, and is sufficiently powerful to be employed for observations on the rotation of the plane of polarisation of light. I had it fitted with an accurately closing glass case, and with adequate arrangements for the proper suspension of the bodies under examination. I am not possessed of instruments which would enable me to determine directly the strength of the magnetic field employed in my several sets of experiments. The Rev. F. J. Jervis-Smith, F.R.S., Millard Lecturer in Experimental Mechanics in the University of Oxford, to whom I had the pleasure of showing my experiments, had the great kindness to make careful measurements of the coils, and has practically re-constructed an electro-magnet similar in dimensions to mine, with the same windings, and of which the iron core derived from a similar instrument made by Ladd, was probably identical in properties to that in my electro-magnet. Using Professor Rowland's method for determining the field, he obtained the following results:—

Intensity of the earth's horizontal magnetic component at Oxford = 0.18.

Distance between faces of pole pieces, 3 c.m.

* In 1874, Dr. R. C. Shettle, in a paper read before the Royal Society (*Roy. Soc. Proc.*, 1875, vol. xiii., pp. 116–120), gave the results of experiments which had led him to the conclusion that arterial blood is paramagnetic as compared with venous blood, which is diamagnetic, the assumed difference in magnetic behaviour being explained by the author as to the paramagnetic properties of the oxygen absorbed by venous blood. In reference to these statements the only observation which I have to make, on the basis of my own work, is that they are entirely erroneous.

* A Paper read before the Royal Society, June 20, 1901.

† De la Rive and Brunner's researches are only known to me at second-hand from the account given of them in Valentin's "Grundriss der Physiologie" (4 Auflage, 1855, p. 507), where an engraving is reproduced in which a bound-up frog is shown placed between the poles of the electro-magnet.

‡ Plücker, "Experimentale Untersuchungen über die Wirkung der Magnete auf gasförmige und tropfbare Flüssigkeiten." Refer to the heading "Über das magnetische und diamagnetische Verhalten der tropfbarflüssigen Körper," in *Poggendorff's Annalen der Physik und Chemie*, 1848, vol. lxxiii., para. 49, p. 575.

Current in ampères.	Magnetic field in C.G.S. units.
2.4	516
3.3	700
4.2	870

Probably it is safe as an approximate estimate to assume that my field was about 1000 C.G.S. units with a current of 5 ampères.

All the fundamental experiments on the magnetic properties of oxy-hæmoglobin, CO-hæmoglobin, and methæmoglobin were made by suspending cakes of the dried crystalline bodies by means of one or a few fibres of silk between the poles, thus avoiding the disturbing influence of glass tubes, however feebly magnetic. In the case of hæmin the substance was similarly examined, in the first instance, by suspending as far as possible rectangular cakes formed by the aggregation of crystals. In the case of hæmatin, the substance being in an amorphous pulverulent condition, was necessarily examined in glass tubes, but its intensely magnetic properties prevented in its case, as in that of hæmin, any difficulties arising from the very feebly magnetic properties of the glass tube containing it.

4. Oxy-hæmoglobin a strongly Diamagnetic Body.

The oxy-hæmoglobin employed in the present research was prepared by myself during the past winter from the blood of the horse by employing substantially the method of Hoppe-Seyler. In some cases the blood corpuscles were separated from the defibrinated blood by long continued centrifugalising; generally, however, the defibrinated blood was mixed with ten times its volume of a mixture made by diluting 10 volumes of saturated NaCl solution with 90 volumes of distilled water, and the corpuscles were then separated by means of the centrifuge.

In either case, the magma of corpuscles were treated with a small quantity of distilled water and pure ether, and the mixture having been thoroughly agitated in a stoppered separating funnel, the aqueous solution of the blood-colouring matter was separated, and filtered into flasks surrounded with ice, and subsequently treated with one-fourth of its volume of pure absolute alcohol at a temperature of -5°C ., and the mixture placed in an ice chamber for twenty-four or thirty-six hours. The oxy-hæmoglobin which crystallised was separated from its mother-liquor by means of the centrifuge. The crystalline mass was repeatedly washed with distilled water at 0°C ., and the washed crystals treated with distilled water at 30°C .; the saturated solution was rapidly centrifugalised, rapidly filtered into flasks surrounded by ice and salt, and the hæmoglobin caused to crystallise by the addition of absolute alcohol under the prolonged influence of cold. After being crystallised three times, the oxy-hæmoglobin was collected on filters, and the moist mass of microscopic crystals drained. The pasty crystalline mass was dried *in vacuo* over sulphuric acid at a temperature which never exceeded 5°C .

Behaviour in the Magnetic Field.—An irregular mass of three times crystallised oxy-hæmoglobin dried *in vacuo*, weighing 1.088 grms., and measuring 18 m.m. in length, 13 m.m. in depth, and 13 m.m. in breadth, was suspended by a couple of fibres of unspun silk between the poles of the magnet, the distance between these being 20 m.m.; the mass was made to rest in the axial position before the current was passed through the coils.

Three cells of an accumulator were employed; on closing the key the mass of hæmoglobin instantly assumed the equatorial position. The experiment was repeated with masses of hæmoglobin prepared at various times, and re-crystallised from one to three times, and weighing from 0.5 to 2 grms., and invariably they were found to be powerfully diamagnetic.

A specimen of oxy-hæmoglobin of the horse, kindly prepared for me under the direction of Professor Hofmeister in the Chémico-Physiological Laboratory of the University

of Strasburg, by the ammonium-sulphate method, and which had been five times crystallised, proved to be as powerfully diamagnetic as the oxy-hæmoglobin prepared by Hoppe-Seyler's method.

5. Carbonic-oxide-hæmoglobin is, like Oxy-hæmoglobin, strongly Diamagnetic.

Mode of Preparation.—The carbonic oxy-hæmoglobin employed was prepared by saturating a concentrated solution of twice crystallised oxy-hæmoglobin with pure CO, and then crystallising the CO compound by the addition of absolute alcohol and exposure to a temperature of -5 to 10°C .

Behaviour in the Magnetic Field.—A nearly rectangular prismatic mass of CO-hæmoglobin which had been dried *in vacuo*, and which weighed 0.642 grm., and of which the length was 17 m.m., the breadth 6.5 m.m., and the depth 13 m.m., was brought into the axial position between the poles of the electro-magnet, the distance between these being 18 m.m. On passing the current from three cells of an accumulator through the coils of the electro-magnet the mass instantly assumed the equatorial position. The experiment was repeated with different specimens of CO-hæmoglobin, and invariably with the same result.

In the absence of all data as to the diamagnetic moment of either oxy- or CO-hæmoglobin, it is impossible to state whether these bodies differ in any degree in respect to their behaviour in the magnetic field. Working carefully but merely qualitatively, it would appear, however, that their behaviour in the magnetic field is identical.

6. Methæmoglobin is, like Oxy-hæmoglobin, strongly Diamagnetic.

The substance was prepared by adding to a saturated solution of twice crystallised oxy-hæmoglobin of the horse a few drops of solution of ferricyanide of potassium until the characteristic change in colour and in the spectrum indicated the complete conversion into methæmoglobin. The solution was cooled to -5°C ., treated with one-fourth of its volume of absolute alcohol at -10°C ., and the mixture placed in ice and salt for a period of thirty-six hours. The crystalline methæmoglobin which separated was then washed with repeated quantities of ice-cold water, collected on a filter, drained, and dried *in vacuo* at a temperature not exceeding 5°C . Experiments with lumps of this substance varying in weight between 0.3 and 1.0 grm. showed it to be apparently as diamagnetic as oxy-hæmoglobin.

6. Hæmatin and Acethæmin (Hæmin)—Intensely Magnetic Substances. Preliminary Remarks.

The more recent analysis of Jaquet, Zinoffsky, and Hüfner have led to the conclusion that, at any rate in the horse, the dog, the ox, and the hen there exists a remarkable constancy in the proportion of the iron which exists in hæmoglobin (0.335 per cent.).* If it be assumed that 1 molecule of hæmoglobin contains 1 atom of iron, the molecular weight of the hæmoglobin of the dog, the horse, the ox, and the hen would be 16,669, a result which concurs admirably with the volume of oxygen and carbonic oxide which can enter into combination with hæmoglobin on the assumption (first of all advanced by Lothar Meyer) that 1 molecule of hæmoglobin can combine either with a molecule of oxygen or of carbonic oxide. The empirical formula for the hæmoglobin of the dog calculated by Jaquet from his analysis is probably very near the truth, namely, $\text{C}_{75}\text{H}_{1203}\text{N}_{195}\text{S}_3\text{FeO}_{218}$.

Why should hæmoglobin possess so enormously high a molecular weight? The question suggested itself to Bunge, who has furnished us with a reason which is eminently suggestive:—"The enormous size of the hæmo-

* For a discussion of all the more recent analyses of hæmoglobin, see my article on "Hæmoglobin" in Schäfer's "Text-book, Physiology," p. 199, *et seq*.

globin molecule," says this writer, "finds a teleological explanation, if we consider that iron is eight times as heavy as water. A compound of iron, which would float easily along with the blood current through the vessels, could only be secured by the iron being taken up by so large an organic molecule."

When oxy-hæmoglobin is subjected to the action of acids and alkalis it splits up with great ease into a coloured iron-containing body, and into an albuminous body (or mixture of such bodies). The former, to which the name of Hæmatin has been given, is a derivative of the molecular group existing in the blood-colouring matter, upon which its colour, its spectroscopic characters, and its physiological properties doubtless depend, though it is a derivative which is unquestionably a product of oxidation, and in no sense represents the real hæmochromogen. According to Hoppe-Seyler, the empirical formula of hæmatin is $C_{34}H_{35}O_5N_4Fe$, whilst according to Nencki its composition is represented by the formula $C_{32}H_{32}O_4N_4Fe$.

When the decomposition of oxy-hæmoglobin is effected by glacial acetic in the presence of alkaline chlorides, a perfectly crystalline substance separates, which has been hitherto known under the name of hæmin, but which we shall now, following the suggestion of Nencki, term *acethæmin*. This body was looked upon by Hoppe-Seyler as a hydrochloride of hæmatin; the recent researches of Nencki and Zaleski have shown that acethæmin contains 8.59 of iron, and possesses a composition represented by the formula $C_{34}H_{33}O_4N_4ClFe$; it contains an acetyl group, and both the acetyl and chlorine in it are linked to the iron. When this body is dissolved in weak solutions of sodium hydrate in the cold, the chlorine and acetyl are separated, and on neutralisation with acids, hæmatin of composition $C_{32}H_{32}O_4N_4Fe$ is obtained. It is with these two coloured iron-containing decomposition products of hæmoglobin, hæmatin, and acethæmin that my observations have been carried out. Before referring to these in detail, I wish again to insist that these oxidation-products in no sense represent the unaltered iron-containing group to which the blood-colouring matter owes its physiological properties. As Hoppe-Seyler showed, when hæmoglobin is decomposed by acids and alkalis in the absence of all traces of oxygen, hæmatin is never formed, but a colouring matter which possesses the same spectrum as that which had previously been described by Stokes as that of reduced hæmatin.

This substance Hoppe-Seyler called hæmochromogen, and he expressed the opinion that it constitutes the veritable colour radical upon which the physiological properties of hæmoglobin depend. The experimental facts advanced by Hoppe-Seyler have always appeared to me absolutely inadequate to warrant this hypothesis, which, however, is most suggestive, and demands a thorough and a new investigation.

A. Magnetic Properties of Acethæmin.

The acethæmin employed in the present research was prepared by me from ox's blood by the method of Schalfjew. Some of the specimens were purified by re-crystallisation from glacial acetic acid, others by dissolving in a chloroformic solution of pure quinine, and subsequently adding to the filtrate hot glacial acetic acid, saturated with NaCl.*

My first observations were made with a block of agglomerated hæmin crystals weighing 0.6455 grm., and measuring 26 m.m. in greatest length, 18 m.m. in height, and 6 m.m. in thickness; this block was suspended by two fibres of silk, so as to occupy the equatorial position in reference to the pole pieces of the magnet. The distance between the poles being 30 m.m., on passing a current from three accumulator cells through the coils,

the mass instantly assumed the axial position, and was strongly attracted to the nearest pole, the suspending silk fibres being sensibly deflected from their original vertical position. Even when the poles of the electro-magnet were 40 m.m. apart, the mass instantly set in an axial position when the current was passed. The observations were repeated with numerous specimens of hæmin, and always with similar results.

B. Magnetic Properties of Hæmatin.

The hæmatin employed in these researches was prepared by dissolving re-crystallised and perfectly pure acethæmin in a weak solution of chemically pure sodium hydrate at ordinary temperatures, and precipitating the filtered solution without delay by neutralising with dilute sulphuric acid. The precipitated hæmatin was thoroughly washed, drained, and dried. In consequence of its absolutely amorphous pulverulent character, my magnetic observations on this body were conducted with the aid of tubes of very feebly magnetic glass, containing from 0.1 to 0.4 of pure hæmatin. The intensely magnetic character of hæmatin was as easily demonstrated as had been that of acethæmin.

7. Preliminary Observations on the Electrolysis of Solutions of Pure Oxy-hæmoglobin and CO-hæmoglobin.

The remarkably definite results of my research, which had shown that oxy- and CO-hæmoglobin are decidedly diamagnetic substances, whilst their iron-containing derivatives, acethæmin and hæmatin, are powerfully magnetic, naturally led me to speculate on the possible cause of these differences. It appeared to me that if hæmoglobin were found to be an electrolyte, apart from the interest which would attach to the discovery of the fact, a study of the products of its electrolysis might throw great light upon the question. Do we not know, for instance, that those compounds in which iron and other magnetic metals are present in electro-negative radicals are diamagnetic?*

In spite of my having made great efforts to purify as completely as possible the substances with which I worked, it is questionable whether their purity was sufficient for electrolytic researches. The experiments which I have yet made on this division of my subject must therefore be looked upon as strictly preliminary, and I hope in the course of the coming winter to extend them greatly, making use of compounds of hæmoglobin which have been subjected to far more frequent re-crystallisation. In the course of these experiments, beside studying the proximate products of electrolysis with currents of different strength and potential, I intend to determine by the methods of Kohlrausch and Ostwald, with as great accuracy as possible, the specific conductivities of solutions of oxy- and CO-hæmoglobin.

The following are the results of my electrolytic experiments which I wish at present to place on record:—

Firstly. When solutions of pure oxy-hæmoglobin are subjected to electrolysis at a temperature of about 15° C. between platinum electrodes, from twelve to sixteen cells of a carbon zinc bichromate battery being employed, and the current passing through the liquid being from 3 to 5 milliampères, a rapid subsidence of the colouring matter takes place, the upper layers of the solution becoming perfectly colourless. The depositing colouring matter retains the spectroscopic character of oxy-hæmoglobin, and when stirred with it is absolutely and almost instantaneously soluble in the liquid from which it has separated. Exactly the same result occurs in the case of carbonic-oxide-hæmoglobin.

Secondly. On continuing the passage of the current through the solution in which precipitation has occurred,

* Refer to my previously quoted article in Schäfer's "Text-book of Physiology," and to Nencki and Zaleski's recent article, "Untersuchungen über den Blutfarbstoff." I. Ueber die Aether des Hämins." *Zeitschrift für Physiologische Chemie*, 1900, vol. xxx., p. 384, et seq.

* Miller, "The Elements of Chemistry," Part I., "Chemical Physics," p. 422, London, 1855; H. du Bois, "Propriétés magnétiques de la matière pondérable. Rapports présentés au Congrès International de Physique réunis à Paris en 1900," Paris, 1901, Tome II., p. 460.

secondary reactions occur, gas is developed both at the anode and cathode, and in many cases a dirty white-brown deposit forms at the cathode.

Thirdly. Under conditions of strength of current and potential which were not determined with sufficient accuracy, and which I have not yet been able to reproduce at will, the solutions of oxy-hæmoglobin and CO-hæmoglobin have, under the long continued action of the current, on several occasions deposited at the anode an insoluble red colouring matter containing both the albuminous and the iron-containing residues of hæmoglobin. In the case of CO-hæmoglobin the compound deposited has presented the peculiar colour of CO-hæmoglobin.

8. General Conclusions.

The following are the conclusions to which I have been led by my experiments.

1. The blood-colouring matter, oxy-hæmoglobin, as well as carbonic-oxide hæmoglobin, and methæmoglobin, are decidedly diamagnetic bodies.

2. The iron-containing derivatives hæmatin and acethæmin are powerfully magnetic bodies. The differences in magnetic behaviour between the blood-colouring matter and acethæmin and hæmatin point to the profound transformation which occurs in the hæmoglobin molecule when it is decomposed in the presence of oxygen.

3. The preliminary study of the electrolysis of oxy-hæmoglobin and CO-hæmoglobin renders it probable that, in the blood-colouring matter, the iron containing group, on which its physiological properties depend, is (or is contained in) an electro-negative radical; according to analogy, the iron in such a compound would possess diamagnetic and not magnetic properties.

In conclusion, I beg to acknowledge my indebtedness to Professor von Bunge, of Basel, to Professor Franz Hofmeister, of Strassburg, and to Dr. v. Ehrenberg, the technical director of the chemical factory of Messrs. Merck, of Darmstadt, for their great courtesy and kindness in placing at my disposal preparations of hæmoglobin prepared by themselves or under their direction.

RADIO-ACTIVITY OF RADIUM SALTS.

By P. CURIE and A. DEBIERNE.

We have already shown that it is possible to communicate radio-active properties temporarily to any body by means of radium salts, and in particular such properties can be given to distilled water.

Water can be rendered radio-active by several methods. It is possible, for example, as we have already shown, to separate by distillation in an absolutely air-tight vessel the water from a solution of radium chloride several days old. The distilled water thus obtained is strongly radio-active.

A second method, still simpler, consists in placing two crystallising vessels into a closed space, one containing a solution of a radium salt, and the other distilled water. After a time the distilled water becomes radio-active, the radio-activity having been communicated by the gas in the closed vessel.

Finally, a third method consists in enclosing a solution of radium salt in a hermetically sealed celluloid capsule, and plunging this capsule into another closed vessel of distilled water. Under these conditions the celluloid plays the part of a perfectly semi-permeable membrane, and no trace of salt passes through the walls, whilst the activity of the solution is to a great extent communicated to the external water. This induced activity cannot be transmitted by the air across a wall of dry celluloid, but is easily transmitted if the wall is wetted with a drop of water.

Water can be made very strongly active, and, under certain conditions, even more so than that of the body under the influence of which it is rendered radio-active. When kept in a sealed tube, however, the water loses the greater part of its activity in a few days.

When in an open vessel the loss of activity is much more rapid, and is more rapid according as the surface of contact with the air is increased.

Solutions of radium salts behave in an analogous manner. If a solution is left in an open vessel, the activity is considerably diminished, the diminution being more rapid the greater the area of solution in contact with air. But such a solution differs from radio-active water in that the loss of activity is not absolute, for if the solution, after losing its activity, is placed in a sealed tube, it gradually acquires in the course of ten days or so its original activity.

From these observations we are able to deduce a theory which explains various phenomena of radio-activity. It is necessary to admit that each atom of radium acts as a continual and constant source of radio-active energy without knowing precisely where this energy goes.

The radio-active energy accumulated in a body from a mass of radium tends to dissipate itself in two different ways:—(1). By radiation (rays charged and not charged with electricity), (2) by conduction to a body in contact or transmission from particle to particle through the medium of gases and liquids (induced radio-activity). The loss of radio-active energy of a body, as much by radiation as by conduction, is far greater as the quantity of this energy accumulated in the body increases.

It must be understood that an equilibrium is necessarily established. Radio-active energy accumulated in the body goes on increasing until the double loss of which we shall speak later compensates the continual increase of energy furnished by the radium.

We must consider this point of view as analogous to that which is used during an investigation of calorific phenomena. If, in the interior of a body, a continued and constant evolution of heat takes place, the heat accumulates in the body, and the temperature rises until the loss of heat of the body by radiation and conduction make an equilibrium. By following this analogy we must consider a radio-active tension as analogous to temperature and characterised by intensity of radiation (which up to this point we have considered as giving a measure of the intensity of radio-activity). We can thus define a capacity of radio-activity in an analogous manner to calorific capacity.

The theory which we have just put forward can be made to explain various phenomena. In general, except under special conditions, the activity is not communicated from particle to particle across solid bodies. When a solution is preserved in a sealed tube the loss by radiation only consists in this, and the radio-activity of the solution takes a very high value. If, on the contrary, the solution is placed in an open vessel, the loss of activity from particle to particle by conduction becomes considerable, and when a state of equilibrium is established the radio-activity of the solution is very feeble.

We must also remark that the activity of a solid radio-active body left free to the air does not diminish sensibly, because the propagation of the radio-activity by conduction does not take place across solids, it being only an extremely thin superficial layer which is capable of producing the induced radio-activity. We have proved that a solution of the same salt produces much more intense phenomena of induced radio-activity (twenty times greater) than the salt itself. With a solid salt the radio-active energy accumulates in the salt and is scarcely dissipated at all by radiation. On the contrary, when the salt has been in solution for several days, the radio-active energy is divided between the water and the salt, and if the salt and water are separated by distillation the water contains a great part of the activity, and the solid salt is much less active (ten or fifteen times, for example), than before solu-

tion. When left to itself the solid salt regains little by little its original activity.

The communication of the activity of a radium salt to its water of solution is, however, very slow, and the equilibrium is only obtained at the end of about ten days; if, for example, we evaporate such a solution shortly after it is made, the salt retains a much more considerable portion of its radio-activity.—*Comptes Rendus*, vol. cxxiii., No. 5, July 29, 1901.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc. R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.
(Continued from p. 75).

Antimonial Ores.—Owing to the very fusible and volatile nature of antimony sulphide, and also of the oxide its decomposition gives rise to, it is usual to avoid the roasting of antimonial ores by employing nitre to effect the oxidation. The chief drawback to the use of nitre is the difficulty of regulating the quantity to be employed, which can only be learnt by experience. The adjustment of the quantity of nitre is simplified when one sulphide only is present, but this is a condition of things seldom met with in practice. Many text-books give elaborate formulæ for arriving at the quantity of nitre needed for any particular class of ore, but the best of these frequently fail to give reliable results. A formula may sometimes serve as a rough guide, but practical experience alone will enable the assayer to adjust the proportion of nitre.

The quantity may be approximately determined by fusing 5 grms. of the ore with 100 grms. of litharge and 10 grms. of sodium carbonate. The lead resulting from the fusion is weighed, and from this weight is calculated the quantity of lead which would be obtained from the quantity of ore to be used for assay (usually 50 grms.). Deduct 30 (the weight of lead required to collect the gold) from this result, and divide by 5; the figure obtained gives approximately the quantity of nitre necessary to be added.

The difficulty of adjusting the quantity of nitre is largely dependent on the following fact, that sulphur, and in some cases the metals, are capable of two degrees of oxidation, and whether the lower or the higher oxide is formed by the action of the nitre will depend very largely on the conditions of the fusion. In this connection the character of the slag produced is an important factor. When the slag is acid owing to the presence of much siliceous material in the charge, the sulphur will, in most cases, be eliminated as sulphurous oxide (SO_2), and the lower oxide of the metal be formed. On the other hand, if the slag contains much soda, the tendency will be for the sulphur to be oxidised to sulphate (sulphuric acid, SO_3), and the metal converted to the higher oxide.

Sodium carbonate is the most suitable flux for antimonial ores, as it forms readily fusible compounds with the antimony oxides resulting from the action of the nitre. The quantity of sodium carbonate required for ores consisting mainly of stibnite is about equal to the weight of the ore taken.

When sulphides of other metals are present, borax may be substituted for a part of the sodium carbonate, as it is the best flux for the metallic oxides formed during the process.

Nitre may be employed according to either of the following methods:—

I. To effect partial oxidation.

II. To effect complete oxidation.

In the former case, the quantity of nitre added is sufficient to oxidise a portion only of the oxidisable substances,

the remaining portion being oxidised by the lead oxide with the production of metallic lead, which sinks through the molten mass and collects the gold and silver.

In the second method, usually known as Balling's method, sufficient nitre is added to effect the complete oxidation of the oxidisable substances, a mixture of litharge and charcoal being subsequently added to supply lead for collecting the gold and silver.

Method I. Partial Oxidation.—The following proportions are suitable for an antimonial ore containing about 75 per cent of stibnite, and will act as a guide for the quantity of nitre needed for this class of ores:—

Ore	..	..	..	..	50	grms.
Red-lead	..	..	..	..	100	"
Sodium carbonate	..	..	..	..	40	"
Borax	..	..	..	..	10	"
Nitre	..	..	..	..	30 to 40	"

With cover of powdered salt.

The fusion of charges containing nitre is effected in large crucibles at a comparatively low temperature, care being taken to avoid a sudden increase of temperature, as fusion takes place somewhat quickly and the slags are in most cases very fluid. When effervescence has ceased, and the contents of the crucible have become thoroughly liquid and tranquil, it is advisable to lift the crucible out of the fire, and subject it to a rotary motion in order to thoroughly mix the liquid contents. If this treatment causes effervescence it indicates that the action of the nitre is not complete, and the crucible must be returned to the fire, and the fusion continued.

The button of lead obtained should weigh between 25 and 35 grms., but if below or above this weight, the charge must be modified to produce the required weight.

Experience has shown that, as a general rule, from 0.25 to 0.30 part of nitre are required to oxidise the quantity pyritic material which would act as a reducing agent to produce one part of lead, or, in other words, the addition of 1 gm. of nitre will decrease the weight of the lead button by from 4 to 5 grms. Conversely, the weight of the lead button may be increased by from 4 to 5 grms. by diminishing the quantity of nitre by 1 gm. The weight of lead obtained will vary somewhat according to the quantity and nature of the fluxes used and the conditions of the fusion.

Until experience has been gained, the first assay of an ore of unknown composition may be more or less unsatisfactory, but the result obtained from the fusion will indicate what modification of the charge is necessary to give a satisfactory result.

When insufficient nitre is used the lead button is brittle, and resembles galena owing to the presence of sulphur; it is also frequently accompanied by a layer of regulus.

With due attention, the nitre may be so adjusted that a malleable button, comparatively free from antimony, will be obtained, and may be cupelled direct. If the button is brittle, comparatively hard, and white, it generally contains antimony, in which case it must be scorified with the addition or more lead if necessary before being cupelled.

The slags from comparatively rich ores should be cleaned in the manner already described under basic ores.

Method II. Complete Oxidation (Balling's Method).—By this method a quantity of nitre equal to twice the weight of the pyritic material in the ore is usually sufficient to effect complete oxidation, but in exceptional cases rather more than this amount may be required. Borax and sodium carbonate are added as in the previous method to flux the metallic oxides formed, but the red-lead is omitted. The fusion is conducted as before, and when the action of the nitre is complete, and the contents of the crucible are in tranquil fusion, it is withdrawn from the fire and allowed to cool until the slag begins to thicken. A mixture of 40 grms. of red-lead, 2 grms. of charcoal powder, and 10 grms. of borax is then added, the crucible returned to the furnace, and the charge kept in a molten condition for from ten to fifteen minutes. When

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

all action has ceased, the contents of the crucible are poured into a mould in the ordinary way. By this means the globules of metallic lead obtained by the reduction of the red-lead sink through the molten slag, and collect the gold and silver.

Baling's method of complete oxidation requires a little more time than the method of partial oxidation, but the lead button obtained by the former method is always of the required weight, and is usually comparatively free from antimony, and may generally be cupelled direct. Both methods, however, give equally satisfactory results when due precautions are taken.

Antimonial ores sufficiently rich in gold to allow of comparatively small quantities being used for assay may be oxidised by means of lead oxide instead of nitre. In this case the stibnite is oxidised by the lead oxide with the production of antimony oxide and metallic lead, which latter acts as a collecting agent for the gold and silver ($\text{Sb}_2\text{S}_3 + 9\text{PbO} = \text{Sb}_2\text{O}_3 + 3\text{SO}_2 + 9\text{Pb}$). Stibnite requires from fifteen to twenty times its weight of lead oxide to effect oxidation.

Combined Wet and Dry Method.—The following method, involving solution of the ore, may be conveniently employed for antimonial ores as a check upon other methods. It possesses the advantage of producing lead buttons practically free from antimony, and thus avoiding the necessity of scorification previous to cupellation. The weighed quantity of ore (from 30 to 50 grms.) is treated with concentrated hydrochloric acid, and heated until decomposition is complete; the solution is diluted with a small quantity of water in which a few crystals of tartaric acid have been dissolved. The insoluble residue is allowed to settle, and when the solution is clear as much of the liquid as possible is poured off through a filter without disturbing the residue. The residue is finally transferred to the filter, allowed to drain, and then dried. The filter-paper is burnt, and the ash, with the insoluble residue, is scorified with ten times its weight of granulated lead and a cover of borax, or it is fused with the following fluxes:—

Red-lead 30 grms.
Charcoal powder 1.5 „
Sodium carbonate and borax,
varying together up to .. 30 „

The fusion is effected in the ordinary way, and the resulting lead button cupelled direct.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 77).

PARTIAL nitration ensues on using nitric acid 1.4 alone, even without addition of sulphuric acid. In this case very little oxycellulose is formed (0.0018 grm. methyl-blue per 1 grm.). Hence the cellulose determinations thus carried out may be taken as approximately accurate; they also exhibited fairly good agreement with each other, while, with a larger percentage of oxycellulose, differences up to 10 per cent occur. The cellulose result was 62.87 per cent; 1 grm. of the mixture evolves 23.73 c.c. NO, and from this the calculated amount of the nitrogen of the pure nitration product is 63.92 c.c. NO = 4.00 per cent N. This would correspond to a dinitrocellulose ($\text{C}_{24}\dots$) whose theoretical percentage of nitrogen is 3.96. As this stage of nitration has so far not been obtained in any other way, an attempt was made to really isolate it from the cellulose in order to determine the nitrogen directly. But all attempts with the ordinary organic solvents were unsuccessful, for the solubility is diminished

by the great proportion of unchanged cellulose. We also tried, by repeatedly treating this nitration product with 1.4 nitric acid, to convert the unchanged cellulose into the desired stage of nitration, but without success. Even after the third repetition, the nitrogen percentage, and hence the amount of unchanged cellulose, remained almost constant.

On addition of 5 per cent sulphuric acid to the 1.4 nitric acid, the formation of oxycellulose is increased to nearly double the quantity. In consequence, the cellulose determination is less exact, and shows differences as great as 5 per cent. Taking the higher of the numbers thus obtained as the more correct (58.04 per cent), we obtained for the pure nitration product 81.62 c.c. NO = 5.12 per cent N. The theoretical amount of nitrogen for a trinitrocellulose ($\text{C}_{24}\dots$) would be 5.36 per cent—a stage of nitration not obtained hitherto. But this result is only an approximation, on account of the unavoidable inaccuracy of the cellulose determination. All attempts to isolate the nitration product failed.

On further addition of sulphuric acid, mixtures of nitrocelluloses with unchanged cellulose were again obtained. These experiments are given in the following table:—

TABLE XI.

Expt.	C.c. NO per 1 grm.	Per cent N.	Solubility in ether- alcohol.	In- crease.	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	147.78	9.27	14.22	134	41.86	35.82	22.32
2.	164.50	10.32	92.30	142	38.47	40.19	21.34
3.	171.57	10.76	98.24	151	40.83	38.72	20.45
4.	175.78	11.02	98.90	153	42.92	37.40	19.68
5.	195.00	12.23	99.58	155	48.03	34.18	17.79
6.	203.71	12.77	99.82	166	49.37	33.38	17.25
7.	207.70	13.02	99.32	165	50.71	32.50	16.79
8.	209.10	13.11	7.65	167	52.81	31.27	15.92
9.	214.62	13.45	2.63	173	54.92	30.06	15.02

The ratio of the cellulose to the nitric acid contained in the nitration mixture was 1:25. No unchanged cellulose was discoverable in polarised light in the product obtained in Experiment 1; but no certain conclusion could be drawn from this observation, as the greater part of the structure of the cellulose was destroyed. With iodine and sulphuric acid a brown colouration was next produced, and gradually a feeble blue; therefore it appeared that a small quantity of cellulose was still present. The nitrogen determination gave 147.78 c.c. NO. For isolation of the pure product we made use of a property of the nitration stages below octonitrocellulose discovered by Dr. Brönnert, viz., their solubility in 95 per cent alcohol containing 4 per cent calcium chloride. With this mixture, about 10 per cent was extracted in the cold, and a further amount of 35 per cent with an inverted condenser. The product showed a nitrogen content of 148.68 c.c. NO, differing only by 0.07 per cent from that of the original material. Hence only traces of cellulose could have been present. The portion insoluble in ether-alcohol contained a percentage of nitrogen corresponding to hexanitrocellulose—another proof of the insolubility of this stage of nitration.

Experiments 2—5 include the group of the collodion-cottons, i.e., the stages of nitration between hepta- and enneanitrocellulose.

Experiment 6 gave a product whose nitrogen corresponded exactly to that of decanitrocellulose, and completely soluble. The question has often been raised as to the solubility of this stage of nitration. Eder considers it soluble, Vielle insoluble, and Lunge and Weintraub only obtained an insoluble decanitrocellulose. Thus we see that in this simple manner the question of the solubility of any product of nitration cannot be answered, and the percentage of nitrogen alone affords no definite conclusion as to the solubility in general. The numerous contradictory reports as to the solubility of certain stages of nitration partly originate from products falsely called nitrocelluloses, viz., those whose production is preceded by a

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

solution in acid, or which are obtained by the breaking down of higher stages with alcoholic potash. But, apart from these products, we find still further complications, even in the usual method of nitration with nitric and sulphuric acid at the ordinary temperature. The decanitrocellulose obtained by Vieille by nitrating with pure concentrated nitric acid is insoluble, as also that prepared by Lunge and Weintraub with concentrated nitric-sulphuric acid 10 : 1, while that resulting from Experiment 6, obtained by using a more dilute acid mixture, is soluble. Therefore two forms of decanitrocellulose exist—the soluble and the insoluble.

This is in agreement with the researches of Sir Henry Roscoe, who, by means of the well-known cordite processes, obtained a soluble and insoluble nitro-cellulose with 12·8 per cent N.

Experiment 7 shows that it is not possible to go further in this direction; it yields a nitration product with a nitrogen content of 20·7 c.c. NO, and completely soluble. Soluble products corresponding to decanitrocellulose and higher have also been obtained on the large scale. These are of value in the manufacture of explosive gelatin and other explosive materials, with which it is important to get soluble nitration products with the highest possible percentage of nitrogen. But we see from a conference of the New York section of the Society of Chemical Industry that the conditions for obtaining these highly nitrated soluble products are not universally known; for, on the one hand, a soluble nitrocellulose with 12·9 per cent nitrogen prepared a few months previously is announced as a novelty, and on the other hand, it is asserted that this is accompanied with difficulties.

On further addition of sulphuric acid the solubility quickly diminished. Experiment 9 gave an eleven-fold nitrated cellulose. This result is very remarkable, because the nitration mixture used contained 15 per cent water, and the endecanitrocellulose formerly prepared could only be obtained with concentrated acid mixtures. We thus had cause to proceed further in this direction and obtained higher stages of nitration.

(To be continued).

ON THE METEORIC STONES WHICH FELL NEAR ZOMBA, BRITISH CENTRAL AFRICA, ON JANUARY 25TH, 1899. WITH NOTES ON THE CHEMICAL ANALYSIS OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Continued from p. 83).

Unattracted Material: Third Portion.

35. The trace of undecomposed material which, after treatment with hydrofluoric and sulphuric acids weighed 0·0026 (§ 12), must before that treatment have weighed 0·0032 (§ 19); and the total amount of undecomposed material is 0·0032 + 0·0107 + 0·0241, or 0·0380, for the undecomposed material is not appreciably altered in weight by ignition (§ 18).

The true SiO₂ is thus 0·4208—0·0032 or 0·4176; but of this, 0·0049 is due to the sodic solution itself (§ 13); hence the SiO₂ really due to the silicate is 0·4127.

The Fe₂O₃, Al₂O₃, SiO₂ 0·0069 consists of Fe₂O₃ 0·0037, Al₂O₃ 0·0031 (SiO₂ 0·0001, making the total SiO₂ 0·4128).

Deducting Fe₂O₃ 0·0009 as due to the sodic solution itself, Fe₂O₃ 0·0028 has passed into the sodic solution from the silicate (possibly through finely-divided silicate passing through the pores of the filter).

The Fe₂O₃, Al₂O₃, SiO₂ 0·3775 consists of Fe₂O₃ 0·3755, Al₂O₃ 0·0002 (SiO₂ 0·0018, due to the action on the vessels).

CuS (ignited) 0·0003 and Ni(Co) 0·0010 may be neglected during the calculation.

MnS 0·0056 corresponds to MnO 0·0046.

The Mg₂P₂O₇ (pure) is 1·0958 (§ 12)—0·0054 (§ 20) or 1·0904, corresponding to MgO 0·3948.

The total Fe₂O₃ is 0·3755 + 0·0028 or 0·3783, corresponding to FeO 0·3405; further, 2·0317 of the unattracted material contain an amount of sulphur (§ 7) corresponding to FeS (troilite) 0·1145 which itself corresponds to FeO 0·0936; as this iron is in the acid solution, only 0·3405—0·0936, or 0·2469, of FeO is due to the silicate.

The total CaO obtained is 0·0023 + 0·0107 or 0·0130; from this must be deducted 0·0005 as due to the sodic solution (§ 13).

Also 2·0317 of the unattracted material contain (§ 32) K₂O 0·0017, Na₂O 0·0241; and the 0·8380 of undecomposed material contains (§ 22) K₂O 0·0015, Na₂O 0·0133; hence K₂O 0·0002 (or nil) and Na₂O 0·0108 must have passed into the acid and sodic extracts.

Collecting these results we have:—

		Percentages.
Undecomposed material	 0·8380	41·25
Troilite	 0·1145	5·64
SiO ₂	 0·4128	20·32
FeO	 0·2469	12·15
MnO	 0·0046	0·23
MgO	 0·3948	19·43
CaO.. { Acid extract 0·0107	 0·0125	0·61
{ Sodic extract 0·0018		
Al ₂ O ₃ { Acid extract 0·0002	 0·0033	0·16
{ Sodic extract 0·0031		
K ₂ O	 Nil	Nil
Na ₂ O	 0·0108	0·53
Total	 2·0382	100·32
Weight taken	 2·0317	100·00

36. Bringing the results together for convenience of comparison, we have—

	I.	II.	III.	Mean.	Oxygen.
Undecomposed material	.. 42·13	43·21	41·25	42·20	—
[Troilite	.. 5·63	5·64	5·64	5·64]	—
SiO ₂	.. 19·33	19·65	20·32	19·77	10·47
FeO	.. 11·83	12·06	12·15	12·01	2·67
MnO	.. 0·22	0·23	0·23	0·23	0·05
MgO	.. Undet.	18·72	19·43	19·07	7·59
CaO	.. Undet.	0·42	0·61	0·51	0·15
Al ₂ O ₃	.. 0·19	0·20	0·16	0·18	0·08
[Na ₂ O	.. Undet.	0·50	0·53	0·51]	0·13
Total	.. 79·33	100·63	100·32	100·12	
Weight taken	100·00	100·00	100·00	100·00	

In the analysis of the first portion, the three successive extractions with acid were allowed to proceed for one and a-half hours, two hours, and two hours respectively; in the case of the second portion the times were two hours, one and three-quarter hours, and two hours respectively; in that of the third portion, each extraction lasted two hours. As it has been shown (§ 30) that no less than 11·64 per cent of the undecomposed material are decomposed during such extractions, it follows that the variation from 41·25 per cent to 43·21 per cent in the amount of residue in the three analyses is sufficiently accounted for by variations of circumstances during the extractions; for instance, of the times for which each extraction is allowed to proceed, the temperature of the extracting acid, the frequency of renewal of the evaporated water, and so on. The actual extract corresponds very closely to olivine, and, neglecting the soda and alumina, has the following composition:—

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

	Per cent.		Oxygen.	Muddoor.	Linn County.
SiO ₂ ..	19'77	38'25	20'26	38'32	38'80
FeO ..	12'01	23'23	5'16	23'29	21'31
MnO ..	0'23	0'45	0'10	—	—
MgO ..	19'07	36'89	14'68	36'90	39'89
CaO ..	0'51	1'18	0'34	1'07	—
Al ₂ O ₃ ..	—	—	—	0'42	—
	51'59	100'00		100'00	100'00

This composition is virtually identical with that calculated by Crook ("Die Chemische Natur der Meteoriten," von C. Rammelsberg, 1879, p. 54) for the olive of the Muddoor meteorite, and also is very nearly that of the "decomposed portion" of the Linn County stone as analysed by Rammelsberg (*Monatsb. Ak. Wiss. Berlin*, 1870, p. 459).

Some of the silica, however, must have been originally in combination with the soda and alumina which have been neglected, and further a small quantity of the remaining constituents is due to the action of the hydrochloric acid and sodic solution on the enstatitic silicate.

37. An estimate of the quantities due to the action on the refractory silicates can be obtained by assuming that they are in the same proportion to the undecomposed residue as in the analysis mentioned in § 30. But the estimate will be only approximate, for in the analysis of the mixture the strength of the acid and its decomposing effect are diminished owing to the action of the olive; further, the gelatinous silica from the olive will partially protect the other silicates from the acid; and the presence of the compounds due to the decomposition of the olive may have a disturbing effect on the action of the acid.

These considerations being disregarded, it follows from § 30 that when the residue weighs 88'36 the following amounts due to the refractory silicates have passed into solution:—SiO₂ 6'57, FeO 1'20, MgO 2'03, CaO 0'93, Al₂O₃ 0'67, R₂O 0'24; hence for the residue, 42'20, the corresponding amounts are—SiO₂ 3'14, FeO 0'57, MgO 0'97, CaO 0'44, Al₂O₃ 0'32, R₂O 0'11, making in all 5'55. Deducting these amounts from the quantities found in the solution (§ 36), we have for the less refractory silicate itself:—SiO₂ 16'63, FeO 11'44, MnO 0'23, MgO 18'10, CaO 0'07, Al₂O₃ 0'14, Na₂O 0'40. Omitting the CaO, Na₂O, Al₂O₃ as being possibly extraneous, we have the following composition:—

	Per cent.		Oxygen.	Muddoor (observed).
SiO ₂ ..	16'63	35'84	18'98	35'46
FeO ..	11'44	24'65	5'48	24'36
MnO ..	0'23	0'50	0'11	21'11
MgO ..	18'10	39'01	15'52	38'61
CaO ..	—	—	—	1'13
Al ₂ O ₃ ..	—	—	—	0'44
	46'40	100'00		100'00

The nearness of the oxygen ratio to that of olive is thus lessened by the deduction of the quantities resulting from the action on the refractory silicates; but the composition is almost identical with that observed by Crook for the decomposable silicate of the Muddoor meteorite.

According to this interpretation, the total amount of enstatite, feldspar, and chromite in the unattracted material would be 47'75 per cent, 42'20 per cent remaining undecomposed and 5'55 per cent passing into the acid and sodic solution.

Unattracted Material: Chromite.

38. Since the unattracted material yields 42'20 per cent of undecomposed residue (§ 36), and the latter itself contains (§ 28) 1'45 per cent of chromite, the unattracted material must contain 0'61 per cent of chromite. By direct extraction with hydrofluoric and sulphuric acids only 0'35 per cent was isolated, but probably some is decomposed and passes into solution (§ 6). Similarly, the

chromium obtained during the determination of the alkalis corresponds to only a small fraction of the total chromite (*Mineralogical Magazine*, 1894, x., 307).

39. The enstatite and oligoclase of the unattracted material will thus (§§ 37, 38) amount to (47'75-0'61) or 47'14 per cent, and this will consist (§ 28) of 37'65 of enstatite and 9'49 of oligoclase; the troilite is 5'64 per cent (§ 36); hence the olive amounts to 46'61 per cent. The mineral composition of the unattracted material (neglecting minute quantities of nickel-iron and schreibersite) will therefore be—

	Total weight.	
	Grms.	
Olivine	46'61	5'7894
Enstatite	37'65	4'6764
Oligoclase	9'49	1'1787
Troilite	5'64	0'7005
Chromite	0'61	0'0758
	100'00	12'4208

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

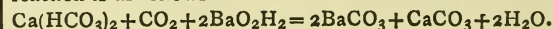
(Continued from p. 81).

Pettenkofer's and Trillich's Methods.

THE estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

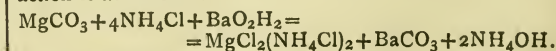
The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows:—



As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate (MgCO₃) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate—or, in fact, any magnesium salt—causes the calcium or barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows:—



An equivalent amount of ammonium hydroxide being formed, no change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in not attempting to prevent the reaction between the magnesium salts and the caustic alkali by the addition of ammonium chloride, but in allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium or calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1.1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulty arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates, and titrates it with hydrochloric acid and cochineal. From this he obtains the "total carbonic acid." By subtracting the "free and half-bound carbonic acid" from this, he obtains the "fixed carbonic acid"; and by finding the difference between the "free and half-bound acid" and the "fixed" (equivalent to the half-bound), he estimates the "free carbonic acid."

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted. Moreover, it would seem more simple to use a method which would not involve the objectionable titration of the suspended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of a separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used, Trillich recommends that to each 9 grms. of the barium hydroxide, 0.5 gm. of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius as follows ("Quantitative Chemical Analysis," p. 405, English edition, 1889):—

"If . . . a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analysed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 c.c. of the water to be analysed, placing it in a bottle, adding 3 c.c. of barium chloride, 2 c.c. of a saturated solution of ammonium chloride, and 45 c.c. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments, an approximately

0.02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0.05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 c.c. of barium chloride in place of 3 c.c., omitting the ammonium chloride, and using phenolphthalein as the indicator. In titrating the suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results:—

1. The barium hydroxide solution (9 grms. $\text{BaO}_2 \cdot 2\text{H}_2\text{O}$ and 0.5 gm. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per litre) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A syphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0.6 per cent weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested, as it deteriorates rapidly. A solution containing 2.8636 grms. per litre (1 c.c. = 1 m.grm. CO_2) was found at the end of forty-five days to be 6.7 per cent weaker, and one fifty days old was 8.7 per cent weaker.

3. Dry or well drained ground-glass stoppered bottles, with their stoppers well vaselined, should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analysed should properly, if at all high in free and half-bound carbonic acid, be introduced into the bottle by means of a syphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tip on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be run in as quickly as possible, and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours, and under no conditions should the stopper be removed until the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 c.c. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important, and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow-mouthed fairly long-necked flask, preferably of about 250 c.c. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle, and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected, the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly, it is better to run into the empty flask the larger portion of the acid, and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air, and consequently any carbonating of the barium hydroxide.

10. The standardisation of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample.

In standardising the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method that the titration should take place in the presence of ammonium chloride, if rosolic acid, or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous, and the differences, though slight, will lead to considerable error.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined chemically by us during July, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month shows an excess for the first time since April. The actual rainfall measured was 4.66 inches, of which 4.33 inches fell on the 24th, 25th, 26th, and 27th. The average fall for the month of July is only 2.49 inches; this gives an excess of 2.17 inches on the thirty-five years' average, and reduces the previous deficit for the year to 0.13 inch, or 0.9 per cent.

Our bacteriological examinations of 477 samples have given the results recorded in the following table; we have also examined 111 other samples, from special stand-pipes, houses, &c., making a total of 588 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	383
New River, filtered (mean of 119 samples) ..	13
Thames, unfiltered (mean of 27 samples) ..	5560
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 245 samples) ..	35
Ditto ditto highest	360
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	837
River Lea, from the East London Company's clear-water wells (mean of 34 samples) ..	40

Out of the total number of samples of filtered water collected and examined, 59 samples gave such abnormally high results that they are excluded altogether, and are dealt with in our subsequent remarks.

Of the remaining 398 samples of impounded and filtered

water supplied to London and examined bacteriologically during the past month, 9 samples, or 2.2 per cent, were sterile. Ten samples contained more than 150 microbes, and 31 samples, or 7.7 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the excess samples was 173, against a corresponding mean of 155 in June.

We have pointed out on previous occasions that during the summer months, when the rainfall is small, the river Thames mainly consists of spring water derived from the large deposits of chalk in the upper Thames valley.

For the last six years the bacteriological examination of the London water supply has shown an exceptionally high degree of purity during the summer months, and this year also, during June and the first week of July, we have enjoyed the normal bacterial purity of the dry summer supply. But between the 6th and the 15th of July, nearly the whole of the filtered water of the different companies, derived from the valleys of the Thames and Lea, showed an excessive number of microbes per cubic centimetre, far above the variations permissible as showing the difference between good and bad filtration. After the 15th of July the supply rapidly reassumed its usual high quality.

This abnormal development of microbes in the filtered water would appear to be due to some exceptional climatic conditions, favouring, in all probability, the development of vegetable spores of a harmless character, because, after careful examination we have satisfied ourselves that there has been nothing very unusual in the general rate of filtration, the mode of taking samples, or the method of testing. The fact that this microbial outbreak was general throughout all the Companies is a proof that it could not be due to any want of care in the filtration, for it would be impossible to conceive that all the Companies simultaneously were using defective filters, or filtering at an excessive rate. Moreover, during these nine days the raw Thames, Lea, and New River waters were exceptionally good, and therefore the difficulty of dealing with their further purification should have been, with efficient supervision, less than during other times of the year.

On minute examination of the microbes we could discover none of a pathogenic character; no did we find the microbe associated with decomposing animal matter, viz., *Bacillus coli communis*. There were undoubtedly liquefying organisms occasionally present, and minute bacteria such as do not usually occur amongst ordinary river microbes. A similar unexplained bacterial outburst was recorded by Sir Edward Frankland and ourselves during the severe winter of 1894-5.

During the latter part of the month of July the Thames valley was visited by an exceptionally high rainfall, and in consequence the unstored, crude, Thames water has become from twelve to fifteen times worse bacterially. But in spite of this the London supplies have resumed their normal character; again proving that the microbic purity of the supply is substantially independent of the condition of the running river.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

Action of Silver on Hydrobromic Acid and the Inverse Reaction.—M. Jouriaux.—An investigation of the action of silver on hydrobromic acid gives results which are in general parallel to those which the author obtained whilst examining the action of silver on hydrochloric acid. The experiments were conducted at about 600° in sealed tubes, the hydrogen being under varying pressures. The influence of temperature on the limits of the two inverse reactions $\text{Ag} + \text{HBr} \rightleftharpoons \text{AgBr} + \text{H}$ was examined, the limits of temperature being 0° and 700°.—*Comptes Rendus*, cxxxiii., No. 4.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A SUMMARY).

By HARRY C. JONES.

THE question of the dissociating power of different solvents is one of the most important in physical chemistry to-day. The first step in the study of the physical chemistry of any solvent is to determine accurately its dissociating power, in order that the knowledge obtained may not be simply qualitative but quantitative.

It has often been pointed out that physical chemistry, until quite recently, was almost exclusively the physical chemistry of aqueous solutions. This is due to the fact that water is a good solvent for many substances, that it can be easily obtained in a high degree of purity, and kept free from other solvents, and further, that the dissociating power of water can be easily measured. In the last few years, however, a beginning has been made with other solvents, and the first step—the measurement of their dissociating power—taken, at least approximately in a number of cases.

The question of the dissociating power of solvents has acquired additional interest because of certain theories which have been proposed, connecting this property of solvents with other properties, chemical and physical. Thus, J. J. Thomson (*Phil. Mag.*, xxxvi., 320), and also Nernst (*Zeit. Phys. Chem.*, xiii., 531), have proposed the theory that the dissociating power of solvents should be very closely connected with their dielectric constants. Brühl (*Zeit. Phys. Chem.*, xviii., 514; xxvii., 319; xxx., 1; *Ber. d. Chem. Ges.*, xxx., 163; xxviii., 2847; and xxviii., 2866), thinks that water and similar substances are non-saturated compounds, and refers the large association of their molecules (shown by the surface-tension method of Ramsay and Shields), as well as their large dielectric constant and high dissociation power, to this cause. Ciamician (*Zeit. Phys. Chem.*, vi., 403), thinks that dissociation is a chemical function of the substance, and those compounds which resemble one another chemically, as water, methyl alcohol, &c., should have the greatest dissociating power. While Konowalow (*Wied. Ann.*, xlix., 733), holds the opinion that only those solutions conduct where there is a chemical action between the solvent and the dissolved substance.

The work which has been done will be considered under the following heads:—Inorganic solvents, organic solvents, and mixed solvents.

Inorganic Solvents.

Water.—The dissociating power of water has been determined for a large number of substances, by several different methods. The more general methods are:—The conductivity method of Kohlrausch (*Wied. Ann.*, xxvi., 160), and the solubility method of Nernst (*Zeit. Phys. Chem.*, iv., 372), and Noyes (*Zeit. Phys. Chem.*, vi., 241; ix., 603; xii., 162; xvi., 125), and the freezing-point methods of Jones (*Zeit. Phys. Chem.*, xi., 110, 529; xii., 623), Loomis (*Wied. Ann.*, li., 500; lvii., 495; 591; lx., 523), and others.

The results obtained by all of these methods agree to within the limit of experimental error. Water, as we shall see, has the highest dissociating power of any solvent thus far obtained in the pure state, and it is probable that there is only one other substance known which, under similar conditions, can ionise substances to the same extent as water.

To determine the dissociating power of solvents other than water, the conductivity method has thus far been chiefly used. In order that the conductivities in other

solvents may be compared with those in water, the results for a typical acid, base, and salt in aqueous solution are given. The following measurements were made at 18°. The volume v is the number of litres which contains a grm.-molecular weight of the electrolyte. μv is the molecular conductivity at the volume v .

Hydrochloric acid.		Potassium hydroxide.		Potassium chloride.	
v .	μv .	v .	μv .	v .	μv .
0.1	60.0	0.1	42.3		
0.2	142.0	0.2	99.0		
0.333	201.0	0.333	131.4	0.333	82.7
1.0	278.0	1.0	171.8	1.0	91.9
10.0	324.4	10.0	198.6	10.0	104.7
100.0	341.6	100.0	212.4	100.0	114.7
500.0	345.5	500.0	214.0	500.0	118.5
1000.0	345.5	1000.0	213.0	1000.0	119.3
				5000.0	120.9
				10000.0	120.9

The percentage of dissociation, α , at any dilution is obtained by dividing the value of μv at that dilution by the maximum value of μv for the substance which is called μ_{∞} .

In most solvents it is impossible to determine the value of μ_{∞} directly by the conductivity method, since the dilution at which μ_{∞} is reached would be so great that it would not be practicable to apply the conductivity method to it. The best that can be done in such cases is to determine the values of μv for varying dilutions and then compare these with the corresponding values in water. In this way an approximate idea of the dissociating power of different solvents can be obtained.

Ammonia.—That solutions of salts in liquid ammonia conduct the current was shown several years ago by Cady (*Journ. Phys. Chem.*, i., 707). Goodwin and Thompson (*Phys. Rev.*, viii., 38), also made some measurements of the conductivity of such solutions, in connection with their work on the dielectric constant of liquid ammonia, but the most elaborate investigation in this field is that of Franklin and Kraus (*Amer. Chem. Journ.*, xxiii., 277; xxiv., 83). They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, mercuric cyanide, and a number of organic compounds in liquid ammonia, at dilutions ranging from a few hundred to many thousand litres. A few of their results for three salts are given:—

Potassium bromide.		Ammonium chloride.		Silver iodide.	
v .	μv .	v .	μv .	v .	μv .
301.9	210.6	298.9	159.0	314.1	83.5
932.6	259.5	923.4	208.7	951.3	122.7
4099.0	308.5	4059.0	264.7	4034.0	188.2
21480.9	336.1	21270.0	298.8	18200.0	247.5
65040.0	340.2	64400.0	301.4	55120.0	274.0
78430.0	340.4	77660.0	304.4	80000.0	276.0

A direct comparison of the molecular conductivities of salts in liquid ammonia with the molecular conductivities in water at the same dilutions, will show that the former values are much larger than the latter. This would seem to indicate, at first sight, that ammonia has a greater dissociating power than water, but such is not the case. It will be observed that the conductivities in water are measured at 18°, or 82° below its boiling-point, while the conductivities in liquid ammonia are measured at its boiling-point—38°. The conductivities in liquid ammonia should be compared with the conductivities in water at its boiling-point, and the latter values would be, in many cases, more than double the conductivities in water at 18°.

Further, if the molecular conductivities in liquid ammonia should even be greater than in water under comparable conditions, this alone would not show that the

* *American Chemical Journal*, xxv., No. 3.

dissociating power of ammonia was greater than that of water. The percentage of dissociation,

$$\alpha = \frac{\mu_v}{\mu_{\infty}};$$

μ_v might be larger in ammonia than in water, and the difference between the two values of μ_{∞} might be even greater, so that μ_{∞} would be smaller in ammonia. Such is the fact. The high value of the molecular conductivity in ammonia is due rather to the great velocity with which the ions move through this solvent than to the large number of ions present.

Nitric Acid.—Bouty (*Comptes Rendus*, cvi., 595), has shown that the conductivity of certain alkaline nitrates dissolved in nitric acid is very large, being of nearly the same magnitude as in water. The work is far too incomplete to enable us to draw any conclusion as to the relation between the dissociating power of nitric acid and of water. The dissociating power of the acid is, probably, very great.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 5, July 29, 1901.

The Solubility of Mixtures of Copper Sulphate and Sodium Sulphate.—MM. Massol and Maldés.—Solutions obtained from a mixture of copper sulphate and sodium sulphate (both salts being in excess) possess an invariable composition at low temperatures, as Rüchhoff has already observed, but when the temperature is high enough for the anhydrous modification of sodium sulphate to be formed (from 23—32° according to the nature of the mixture) the composition of the solution varies with the relative proportions of the two salts.

Neodymium Chloride.—Camille Matignon.—Will be inserted in full.

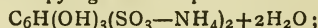
Alloys of Aluminium and Molybdenum.—Leon Guillet.—By the reduction of molybdic acid with aluminium, six compounds can be isolated corresponding to the formulæ Al_7Mo , Al_3Mo , Al_2Mo , $AlMo$, $AlMo_4$, and finally a compound very rich in molybdenum which apparently corresponds to the formula $AlMo_{20}$. The author examines the properties of all these compounds.

Crystallisation of Cerium Oxide.—Jean Sterba.—By a method of crystallisation of cerium oxide at different temperatures the author obtained this substance in cubes or cubo-octahedrons, isotropic, colourless, and transparent, but whose density varies according to the temperature at which crystallisation takes place.

Cæsium.—C. Chabré.—In order to obtain all the metal from the mineral containing cæsium the author suggests the plan of drying the mineral at 130°, grinding it to a fine powder, and reducing it in a platinum crucible with a hundred times its weight of pure hydrofluoric acid. The whole must be brought to boiling point and kept at that temperature until solution is nearly complete. The partial solution is then filtered, and after transformation into carbonate can be evaporated to dryness. The author also obtains in a pure state cæsium sulphite, bisulphite, and hyposulphite.

Pyrogallol Sulphonic Acids.—Marcel Delage.—The author devises a method for the estimation of pyrogallol di- and mono-sulphonic acids, using phenolphthalein as an indicator. He also prepares by double decomposition, between a molecule of a metallic sulphate and a molecule of the barium salt, potassium pyrogallol-monosulphonate,

$C_6H_2(OH)_3SO_3K + 2H_2O$, sodium pyrogallol-monosulphonate, $C_6H_2(OH)_3Na + 2H_2O$, ammonium pyrogallol-monosulphonate, $C_6H_2(OH)_3SO_3(NH_4) + H_2O$, potassium pyrogallol-disulphonate, $C_6H(OH)_3(SO_3K)_2 + H_2O$, sodium pyrogallol-disulphonate, $C_6H(OH)_3(SO_3Na)_2 + 3\frac{1}{2}H_2O$, and ammonium pyrogallol-disulphonate—



also aluminium and magnesium pyrogallol-disulphonate.

Action of Ethylic Alcohol on Barium Ethylate. Synthesis of Normal Butylic Alcohol.—Marcel Guerbet.—Will be inserted in full.

MISCELLANEOUS.

Action of Cupric Hydrate on Solutions of Metallic Salts.—A. Mailhe.—Tetracupric hydrate always gives a mixed basic salt when placed in contact with one of the solutions of chlorides or bromides of the metals mercury, zinc, manganese, cobalt, nickel, cadmium, and lead. The action is slow in the cold, but becomes much more rapid on heating. Several minutes of contact are necessary for the action to be complete. The author intends to investigate the analogous reactions of cupric hydrate on solutions of metallic sulphates and nitrates.—*Comptes Rendus*, cxxxiii., No. 4.

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

Complete Courses of Instruction are provided for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture.

Matriculation and Exhibition Examinations begin September 30th; Lectures begin October 8th, 1901.

Hostels for Men and for Women Students.

Prospectuses on application to the SECRETARY.

REDRUTH SCHOOL OF MINES, CORNWALL.

Session 1901-1902 begins September 11th.

A "Mining Certificate" is awarded to Students passing successfully through the School Course.

PRACTICAL MINING CLASSES, under the instruction of apt. W. HAMBLE (late Government Inspector, South Africa).

SYLLABUS and every information on application to—

THE REGISTRAR.

NOTE THE NEW ADDRESS.

LETCHER & SONS,

27, ST. JAMES'S WALK, CLERKENWELL GREEN, E.C.

Makers of the

NEW PATENT RAPID CHANGE BLOWPIPE.

Write for Lists of BLOWPIPE APPARATUS, &c.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered, at 2s. 6d. per volume.

6 & 7, CREED LANE, LUDGATE HILL, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2179.

CHLORIDE OF NEODYMIUM.

By CAMILLE MATIGNON.

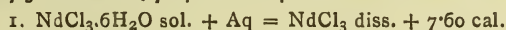
PURE neodymium chloride, crystallised with $6\text{H}_2\text{O}$, was first prepared by Schapleigh and exhibited in the Chicago Exhibition. This substance forms the chief constituent of old neodymium chloride. It is deposited from its hydrochloric solution at ordinary temperatures under the same form, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$.

This chloride is deposited in large, deliquescent, clinorhombic, rose-coloured crystals, of density at $16^\circ\text{C}.$ = 2.282 and with a molecular volume equal to 156.9 .

Chloride of neodymium is very soluble in water. At 13° , 100 parts of water dissolve 246.2 parts of the hydrated salt, or 98.7 parts of the anhydrous salt; 100 parts of the solution contain 49.6 parts of the anhydrous salt and 71.1 parts of the crystallised salt; this solubility increases with the temperature. At 100° , 100 parts of water dissolve 511.6 parts of the hydrated salt and 140.4 parts of the anhydrous salt; whilst 100 parts of the solution contain 58.4 grs. of the anhydrous salt or 83.6 grs. of the hydrated salt.

The saturated solution at 13° has a density equal to 1.741 .

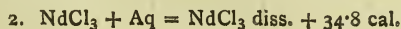
The chloride dissolves in water with evolution of heat. Two experiments made with the chlorides dissolved in water and in hydrochloric acid give respectively the values $+7.58$ cal. and $+7.64$ cal. at 14° :—



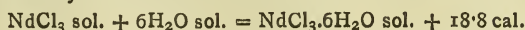
The concentrated solution of chloride possesses the property of dissolving neodymium oxalate easily, and the insoluble oxalates of the other rare earths. On cooling the hot solution, we obtain crystals of oxalo-chlorides, salts whose composition was found by M. Job (*Comptes Rendus*, cxxvii., p. 246). It is impossible to dry the hydrated chloride in the air-oven without a certain amount of transformation into the oxychloride, but decomposition does not take place when desiccation is effected in a current of dry hydrochloric acid gas. Heated under these conditions to 105° , the chloride slowly loses $5\text{H}_2\text{O}$, after which dehydration stops. We have then a new monohydrated chloride, $\text{NdCl}_3 \cdot \text{H}_2\text{O}$.

At 130° , the chloride $\text{NdCl}_3 \cdot \text{H}_2\text{O}$ keeps its water even in dry hydrochloric acid gas, and a temperature above 160° must be attained for the last molecule of water to disappear, and a pure anhydrous salt to be obtained containing no oxychloride.

A very simple method can be devised for preparing anhydrous neodymium chloride—a chloride which was recently prepared by MM. Muthmann and Stützel (*Berichte*, xxxii., p. 3473) by first transforming the sulphate into sulphide in a current of sulphuretted hydrogen, then the sulphide into anhydrous chloride by the medium of hydrochloric acid gas. By this means I easily prepared more than 500 grms. of the anhydrous chloride. The substance thus obtained is in the form of a rose-coloured powder, extremely deliquescent, which melts at a red heat to a liquid, which liquid, on cooling, becomes a rose-coloured transparent mass. It is not perceptibly volatile at a temperature of 1000 — 1100° . When thrown into water, the anhydrous chloride dissolves with a hissing noise, like hot iron. The heat evolved at the moment of solution has been found equal to $+34.80$ cal. at a temperature of 16° :—



By combining the two Equations, 1 and 2, we can deduce the heat of formation of the hydrated salt from the anhydrous salt:—



Absolute alcohol dissolves the anhydrous chloride abundantly. I utilised this property to determine the molecular mass by the variation of the boiling-point of this solvent. Three experiments gave the following values, using the formula $M = K \frac{P}{E}$, where $K = 11.5$.

	E.	P.	M.
	°	Grs.	
I.	0.127	2.74	248
II.	0.154	3.12	233
III.	0.557	11.11	230

The molecular mass for the formula NdCl_3 is equal to 250 ($\text{Nd} = 143.5$). The formula NdCl_2 with $\text{Nd} = 95.6$ would give a molecular mass equal to 166.6 . The formula of neodymium is therefore NdCl_3 if we admit that the quantity of neodymium combined with three atoms of chloride represents a single atom of neodymium.

This hypothesis can be verified by a determination of the lowering of the freezing-point of water containing a small quantity of the chloride in solution. Three experiments have given the following values:—

	Weight of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 parts water.	Lowering observed.	Molecular lowering ($M = 358$).
I.	3.426	0.565	59.2
II.	2.967	0.50	60.3
III.	1.262	0.230	65.5

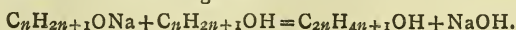
From these results the limit of molecular lowering should be about 66 or 67. This value corresponds exactly to salts consisting of three monovalent acid radicles united to a trivalent metallic radicle. Raoult found, for example, the following limits for salts of the same constitution:— AlCl_3 , 64.5; CrCl_3 , 65; $(\text{NO}_3)_3\text{Al}$, 65.4. Consequently, the molecule of neodymium chloride contains a single atom of neodymium; all the other possible hypotheses do not agree with the preceding numbers. Summing-up the above, I have (1) determined the principal physical constants of neodymium chloride, (2) discovered a new hydrate $\text{NdCl}_3 \cdot \text{H}_2\text{O}$, (3) given a simple method of preparation by means of anhydrous neodymium chloride, (4) shown that neodymium is trivalent in its chloride, and that its atomic mass corresponds to the quantity of metal in this body united to three atoms of chlorine. I may finally add that I have been able to isolate the metal itself by the action of sodium on the anhydrous chloride.—*Comptes Rendus*, vol. cxxxiii., No. 5.

ACTION OF ETHYLIC ALCOHOL ON BARIUM ETHYLATE.

SYNTHESIS OF NORMAL BUTYLIC ALCOHOL.

By MARCEL GUERBET.

I HAVE already read a paper before the Académie, describing the preliminary results of my researches on a new method of synthesis of alcohols, founded on the reaction which takes place at 200° between the alcohols and their sodium derivatives (*Comptes Rendus*, vol. cxxviii., p. 511 and 1002; and vol. cxxxii., p. 207 and 685). At this temperature a molecule of sodium is eliminated between these compounds and an alcohol is formed, which is twice condensed from the original alcohol; the reaction can be expressed in the following manner:—



The soda thus produced reacts immediately on the alcohols, transforming them partially into the sodium salts of the corresponding acids, with evolution of

hydrogen. We thus obtain, with isoamyl alcohol $C_5H_{12}O$; diamyl alcohol, $C_{10}H_{22}O$, and isovaleric acid; with α -naphthyl alcohol, $C_{7}H_{16}O$; β -naphthyl alcohol, $C_{12}H_{20}O$, and α -naphthyl alcohol; with caprylic acid, $C_8H_{18}O$; dicaprylic alcohol, $C_{16}H_{34}O$, and caprylic acid. Ethylalcohol, C_2H_6O , is apparently an exception, because when heated to 210° with its sodium derivative we do not obtain butylic alcohol, $C_4H_{10}O$, as might be expected, but ethylene.

The elimination of the soda, instead of being effected between the alcohol and its sodium derivative as in the case of alcohols of higher atomicity, is simply effected by the sodium ethylate, $C_2H_5ONa = C_2H_4 + NaOH$. I thought that the general reaction, which does not take place with sodium ethylate, might be produced perhaps with barium ethylate, and experiment has confirmed my hypothesis. By heating a concentrated solution of barium ethylate in absolute alcohol to 230° or 240° a small quantity of normal butylic alcohol is produced at the same time as ethylene and hydrogen, besides some acetate and carbonate of baryta. The concentrated solution of barium ethylate is prepared by the method recommended by M. Berthelot (*Annales de Chimie et de Physique*, Series 4, vol. xxx., p. 142). The caustic baryta is dissolved in absolute alcohol in the cold, and the solution brought to boiling-point.

The barium ethylate, less soluble in hot than in cold alcohol, is precipitated and falls to the bottom. The larger portion of the alcohol is now poured off, and the required concentrated solution obtained. This was used for my experiments, and contained 28.5 parts per 100. The solution is divided up into tubes which are sealed, and then heated to 230 – 240° for three days. Each twenty-four hours the tubes are opened to allow the gas to escape, and are then re-sealed.

The gases thus produced are passed through a series of five wash-bottles containing successively water, bromine, a solution of soda, concentrated sulphuric acid, and absolute alcohol, and are then collected over water. The bromine retains the ethylene, the soda the bromine vapours, the sulphuric acid dries the gas, and, finally, the absolute alcohol dissolves eventually any formene which may be formed during the decomposition of barium ethylate, as suggested by M. Destrem (*Annales de Chimie et de Physique*, Series 5, vol. xxvii., p. 23). I may say at once that in my experiments no formene was produced. I found, on the contrary, that a small quantity of ethylene bromide is formed, and analysis of the gas collected over the water shows that it is composed only of hydrogen.

The contents of the sealed tubes are then introduced into a flask and distilled on an oil-bath to dryness. The residue is found to consist of acetate, carbonate of baryta, and unchanged barium ethylate.

The distillate is rectified by the Bel-Henninger method. The whole passes between 76° and 130° , the greater portion between 76° and 80° , and as the first fractions have the precise odour of acetic ether these were all united and boiled with a reflux condenser in the presence of caustic potash to saponify the ethers. The whole is further rectified a great number of times, and a small quantity of liquid separates, boiling at 115 – 117° , the temperature at which normal butylic acid boils, and which substance possesses the composition of this compound (C found to be 62.9 per cent, calculated 63.16 per cent; H found to be 16 per cent, calculated 15.79 per cent).

Finally, to identify this more certainly, 1 grm. was oxidised by means of chromic mixture, and an acid possessing the odour of butyric acid was obtained. We prepared the ammoniacal salt of this, then the amide, and proved that it melts at 114 – 115° , then that normal butyric amide melts at 115° . It has therefore been proved that normal butylic alcohol is formed by the action of ethylic alcohol on barium ethylate at 230 – 240° ; but that the reaction is very slow, and only gives small yields. Using 500 grs. of the concentrated solution of barium ethylate

I only obtained about 3 grs. of butylic alcohol. I remember that the syntheses of diamyl, dicanaphthyl, and dicaprylic alcohols were effected with excellent yields.

The reaction seems to be easier the higher the molecular weight of the alcohol employed.—*Comptes Rendus*, vol. cxxxiii., No. 5.

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc. R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Continued from p. 90).

Cupriferous Ores.—Ores of this class are usually very troublesome to assay correctly by the fusion method, as they are generally poor in gold and silver, and frequently contain a large proportion of copper.

Owing to the readiness with which copper compounds are reduced during the fusion of the ore, some difficulty is experienced in passing the copper into the slag, and thus preventing the formation of cupriferous lead buttons. One part by weight of copper requires about sixteen parts of lead for cupellation, and though a smaller quantity of lead will pass the copper into the cupel, yet a sensible amount of gold and silver would in that case accompany the lead and copper, so that an incorrect result would be obtained (Percy). Under these circumstances it becomes necessary to add enough lead oxide to the charge not only to collect the gold and silver and oxidise the sulphur present, but to yield a button of lead sufficiently large to satisfactorily carry into the cupel all the copper present in the lead. With ores containing much copper this would give rise to the production of lead buttons inconveniently large for cupellation. Reliable results are obtained by direct fusion with ores containing from 20 to 30 per cent of copper, but when larger quantities are present, in most cases it is more satisfactory to remove it by a preliminary treatment with acid.

For this purpose the following method may be conveniently employed:—

From 30 to 50 grms. of the sample (according to the richness in gold and silver), are treated cautiously with fuming nitric acid until the ore is quite decomposed. The solution is warmed to expel all nitrous fumes, and diluted with water; a little hydrochloric acid or salt is then added to precipitate the silver. The solution is stirred well and allowed to settle until the liquid is clear. The supernatant liquid is removed by decantation, the liquid being poured off through a double filter-paper without disturbing the residue. After the liquid has been decanted as far as possible, the residue is transferred to the filter-paper by means of the wash-bottle. The filtrate, which should be bright and clear, contains the copper, and may be neglected. The residue containing the gold and silver is allowed to drain, and then dried, the filter paper burnt, and both added to the following mixture:—

Red-lead	30 grms.
Charcoal powder	1.5 "
Sodium carbonate and borax, varying up to ..	30 " together

The charge is fused in the ordinary way, the resulting button of lead cupelled, and the gold-silver bead parted in nitric acid.

When the quantity of residue is comparatively small it may be mixed with ten times its weight of granulated lead and scorified.

With a view to facilitate the settling of the finely divided precipitate of silver chloride the addition of a lead salt is sometimes recommended.

Preliminary treatment of cupriferous ores with acid, although requiring a greater expenditure of time than

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

direct fusion methods, has the great advantage of producing lead buttons free from copper which may be cupelled direct. When treatment with nitric acid is not adopted, the ore may be assayed by fusion direct or by roasting previous to fusion. The following proportions arrived at experimentally by my father, the late Mr. Richard Smith, of the Royal School of Mines, London, may be taken for the direct fusion of the ore (Percy, "Metallurgy of Gold and Silver," Part I., articles on Assaying by R. Smith, p. 247). The quantity of ore is varied according to the richness in gold, and the percentage of copper present:—

Ore	10 to 50	grms.
Red-lead	200 to 300	"
Charcoal powder	1·5 to 3·5	"
Siliceous sand or glass	10 to 25	"

Charcoal powder is needed in charges for partially oxidised ores, but in the case of sulphide ores it may frequently be omitted, as the sulphur will reduce sufficient lead without it. The red-lead acts as the oxidising agent for the sulphur, but if a large quantity of sulphur is present a little nitre should be added to the above mixture to assist the oxidation. The fusion of the charge is effected in an earthen crucible at a comparatively low temperature. Cupriferous lead is liable to be obtained by this method from ores rich in copper, but when only moderate quantities of copper are present the results are satisfactory.

Hard cupriferous lead buttons should be scorified, with the addition of more lead if necessary, before being cupelled. It is very important that the scorification should be conducted at a low temperature, otherwise the lead is oxidised more rapidly than the copper and the object of the process defeated.

When the ore is roasted previous to fusion the quantity to be assayed, which may vary from 10 to 50 grms., should be weighed out before roasting. The oxidised product is then mixed with the following substances:—

Red-lead	100	grms.
Charcoal powder	3·5	"
Sodium carbonate	20 to 30	"
Borax	15 to 30	"

The quantity of charcoal is varied according to the amount of iron oxide present, as indicated under Basic Ores. The fusion is conducted as before.

In the case of an auriferous antimonial copper ore the following proportions have been found suitable for making an assay by the fusion method of an ore containing about 30 per cent of copper:—

Ore	30	grms.
Red-lead	150	"
Sodium carbonate	120	"
Nitre	18	"

The mixture is fused in the manner indicated under Antimonial Ores for charges containing nitre. The resulting lead button should be sufficiently free from antimony to be cupelled direct; no scoria should be formed on the surface of the cupel.

Ores with Galena and Zinc Blende.—Galena is completely reduced by metallic iron at a red heat with the formation of iron sulphide; consequently iron is the reducing agent generally employed in assaying gold ores containing galena. Ores containing only small proportions of galena may be roasted to effect the decomposition of the sulphide, but owing to the readiness with which lead sulphide volatilises when heated in the presence of sulphur dioxide, great care is needed in regulating the temperature to avoid loss of the precious metal.

If the quantity of galena in the ore is large, the amount of lead oxide added to the charge when fusing the ore may be lessened, or may entirely omitted if sufficient lead will be reduced without it. The fluxing and the fusion of the ore is conducted as described under the desulphurisation of pyritic ores with metallic iron.

Ores containing zinc blende should be roasted previous to fusion.

As this sulphide is practically infusible it tends to diminish the fusibility of other sulphides, such as stibnite and galena, when combined with them. If roasted with access of air zinc blende is decomposed, leaving the oxide which is infusible. Zinc blende is a substance difficult to roast absolutely sweet, although it has but little tendency to clot, and thus permits of a somewhat high temperature being employed in the earliest stages of the roasting. When the roasted product contains a large proportion of zinc oxide, difficulty is sometimes experienced in satisfactorily melting the charge. Zinc oxide combines with silica in definite proportions with the production of silicates difficult to fuse; but with borax and alkaline carbonate the oxide yields readily fusible compounds.

To facilitate the fusion of ores containing much zinc it is necessary to increase the proportion of borax and of sodium carbonate. In exceptional cases a little fluorspar may be added. Desulphurisation with metallic iron may also be employed for ores of this class, and this method is preferred by many assayers, as it occupies less time and obviates any loss of gold and silver which, if due care is not taken, may occur in the roasting operation with ores rich in blende owing to the volatile nature of zinc. In this method an ample supply of sodium carbonate should be used.

Telluride Ores.

Telluride gold ores have received considerable attention at the hands of assayers within recent years owing to the growing importance of this class of ores, and the difficulty of their assay as compared with ordinary ores. The presence of tellurium may be readily detected by the following simple method:—

A small quantity of the ore is heated in an open glass tube whereby a white sublimate of tellurous acid is formed. The portion of the tube containing the sublimate is removed by means of a file, and immersed in a small quantity of strong sulphuric acid in a test-tube. The presence of tellurium is indicated by the characteristic purple colour which it imparts to the acid when dissolved in the cold. The colouration produced by gently heating a small quantity of the ore with concentrated sulphuric acid is of little or no value, as the other minerals commonly associated with tellurium in gold-bearing ores interfere with or conceal this reaction.

A series of assays under varying conditions has been made by Charles H. Fulton (*Journ. Amer. Chem. Soc.*, 1898, xx., 586—597), who has arrived at the following conclusions, which are fully in accord with the author's experience with telluride ores.

For ores of this class scorification of any kind is bad, whether performed direct on the ore, or to reduce large or brittle buttons obtained from the fusion assay. The gold lost in the slag when the ore is scorified direct is very considerable, and there is also loss by volatilisation, the proportion increasing with the richness of the telluride. The crucible assay with direct cupellation is by far the best method, but special precautions are needed in conducting the assay. Telluride ores should on no account be roasted, as this causes considerable loss of gold and silver due to volatilisation.

A large excess of lead oxide is necessary to obtain good results; in the case of rich tellurides the quantity of ore should be decreased rather than the lead oxide increased, so that the lead button may not be too large to cupel directly (20 to 30 grms.). In the presence of lead oxide tellurium is readily converted into telluric acid, which combines with the lead oxide when the latter is in excess ($\text{Te} + 4\text{PbO} = 3\text{Pb} + \text{PbO} \cdot \text{TeO}_3$), but if the contrary be the case the excess of telluric acid is volatilised and telluride of lead is produced. ($2\text{Te} + 3\text{PbO} = \text{TePb}_3 + \text{TeO}_3$).

Experience has shown that the loss of gold is very great if the charge for the fusion is not properly made up as regards the amount of lead oxide. The following charge may be conveniently employed for most telluride ores:—

Ore	50	grms.
Red-lead (according to the amount of tellurium present)	50 to 200	"
Charcoal powder	1 to 2	"
Sodium carbonate	50	"
Borax	20	"
Siliceous sand	10 to 30	"

For very rich ores the following charge should be employed:—

Ore	10	grms.
Red-lead	100 to 150	"
Charcoal powder	1	"
Sodium carbonate	50	"
Siliceous sand	5 to 10	"

The sand is added to diminish the action of the lead oxide upon the earthen crucible. If the ore contain pyritic material, and the quantity of sulphur to be oxidised be large, the charcoal may be omitted, as sufficient lead will be reduced without it.

The whole of the constituents should be well mixed, then charged into the crucible, and covered with a thin layer of powdered salt. For the fusion of the charge the fire should be moderately hot, and the length of time in the furnace from forty to fifty minutes. Great care must be taken to avoid excessive heating at the commencement.

Since the loss of gold in the slag is much greater with telluride ores than in the case of ordinary ores, it is necessary in order to obtain accurate results that the slag should be powdered and re-melted with 30 grms. of red-lead, and 15 grms. of charcoal powder; the button of lead obtained being cupelled. The richer the ore, the more needful is it to clean the slag; in the case of ores very poor in tellurium it may sometimes be omitted. However, in the case of an ore with which the assayer is not familiar, it is better not to omit the examination of the slag until experience has shown that this may safely be done.

The cupellation of the lead is conducted at a low heat with litharge crystals just forming on the cupel. If the lead button is hard or brittle owing to the presence of base metals, and requires scorification previous to cupellation, this should be performed at a comparatively low temperature. When tellurium is present in the lead the gold button obtained from cupellation will be sub-divided into minute particles on the cupel. No difficulty is experienced in obtaining concordant results with telluride ores when due regard is given to the precautions indicated as to the proportion of lead oxide in the charge, and the regulation of the temperature for the fusion of the charge. Rapid fusion invariably gives low results.

(To be continued).

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 91).

C. The Highest Degree of Nitration of Cellulose obtainable by means of Nitric-sulphuric Acid.

On this question there are contradictory reports in print.

Eder obtained with a mixture of 3 parts concentrated sulphuric and 1 part fuming nitric acid a product which was found to contain from 13.74 to 13.91 per cent nitrogen after removing the lower nitration stages by washing with ether-alcohol, and he looks upon this as approximately pure cellulose hexanitrate ($C_{12}...$), i.e., according to our nomenclature, dodecanitrate, which contains theoretically 14.14 per cent nitrogen.

Vieille and Vignon, under precisely similar conditions, obtained products with only 213–214 c.c. NO (13.4 per

cent N), which would nearly correspond to an eleven-fold nitrated cellulose, and they consider this the highest attainable degree of nitration. But, according to Guttman, this percentage of nitrogen might be exceeded, and he agrees with Eder's statement that it is possible to reach the dodecanitrate. Lunge and Weintraub, who worked with numerous proportions of concentrated sulphuric acid to fuming nitric acid, got no further than Vieille, viz., to the maximum of 214.4 c.c. NO. On the other hand, with nitric acid and phosphorus pentoxide, they obtained a product that closely approximated to hexanitrocellulose, with 13.87 per cent N.

The extension of the series of experiments described in the last section led to the following noteworthy results:—

TABLE XII.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture.		
				H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	217.26	13.62	173	60.00	27.43	12.57
2.	219.28	13.75	174	62.10	25.79	12.11
3.	220.66	13.83	175	62.95	24.95	12.10
4.	219.34	13.75	175	63.72	25.31	10.97
5.	218.73	13.71	175	64.36	24.65	10.79

There were therefore now obtained products which approximated to the true hexanitrocellulose (14.14 per cent), more than all former bodies obtained directly from nitric sulphuric acid, viz., up to 13.83 per cent. But it is remarkable that this did not result from the most concentrated acid mixtures, but that those leading to the highest proportion of nitrogen contained relatively much water. Hence our experiments show, not only how higher stages of nitration than those already known can be attained, but also that these are produced by not quite concentrated acid mixtures, and consequently in a proportionately cheap manner.

The importance of this result demanded further research, which was instituted in the following manner:—A mixture of nitric acid 1.5 and sulphuric acid 1.82, in which the ratio of the two acids was the same as in the previous experiments, was diluted with varying quantities of water. The nitrations gave the following results:—

TABLE XIII.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture.		
				H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	219.44	13.76	—	25.28	68.02	6.70
2.	218.95	13.72	173	64.55	26.55	8.88
3.	221.98	13.92	173	63.35	25.31	11.34

Hence, here also, with 11.34 per cent water, a proportion of N near to dodecanitrocellulose can be reached, viz., 221.98 c.c. NO = 13.92 per cent N. This is the highest nitration product of cellulose obtained by direct nitration without washing out the portion soluble in ether-alcohol, and which certainly consists principally of twelve-fold nitrated cellulose ($C_{24}...$).

After a few months, the percentage of nitrogen of a damp sample of this product had sunk to 13.5 per cent. This highest stage of nitration proved to be unstable. On repeating the experiment, we obtained again 13.6 to 13.8 per cent of nitrogen from the first analysis; but in later ones, and after keeping in a desiccator, 13.5 per cent was mostly obtained, and this proportion of nitrogen, corresponding to endecanitrocellulose, remained absolutely constant. This gives a further reason for adopting the formula $C_{24}...$ instead of $C_{12}...$

It might be thought that the possibility, which we have demonstrated, of obtaining by direct nitration unusually highly nitrated celluloses has no practical value, as these products are not sufficiently stable; but, at least, we can conclude from our experiments that the highest practically obtainable degrees of nitration are not produced by the most concentrated acid mixtures, but by one containing a certain quantity of water.

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

The ratio of sulphuric to nitric acid in the previous experiments was 2.50 to 2.52; the following experiments should show whether a change of this ratio within certain limits influences the favourable results obtained:—

1. Ratio of sulphuric acid to nitric acid = 3.3 : 1.

TABLE XIV.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture.		
				H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	215.70	13.53	176	75.33	22.80	1.87
2.	215.54	13.51	175	74.16	22.12	3.72
3.	216.50	13.57	—	72.97	21.63	5.40
4.	217.53	13.64	177	69.90	20.45	9.65
5.	217.10	13.61	176	68.31	20.49	11.20
6.	211.32	13.25	172	67.43	19.37	13.20

2. Ratio of sulphuric acid to nitric acid = nearly 2 : 1.

TABLE XV.

Expt.	C.c. NO per 1 grm.	N per cent.	Increase.	Nitration mixture.		
				H ₂ SO ₄ .	HNO ₃ .	H ₂ O.
1.	217.35	13.62	176.5	67.32	32.53	0.15
2.	216.38	13.57	175	65.41	31.34	3.25
3.	217.50	13.63	176	63.75	30.80	5.45
4.	218.28	13.68	176	70.68	29.31	10.01

Thus, in this case also, rather higher nitration products were obtained with 10 to 11 per cent water than with the concentrated mixtures; it appears therefore, in the latter, that partial saponification of the ester takes place.

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 94).

Pettenkofer's and Trillich's Methods (continued).

In spite of the above precautions, an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vasedin, showed a loss of barium hydroxide equivalent to 1.5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer (*Zeit. Angew. Chem.*, September 15, 1894) found in a solution of lime-water containing 1173.8 parts per million of calcium oxide, carbon dioxide equivalent to (a) 8.7 parts and (b) 9.3 parts respectively. The results were obtained by acidulation of the solution, expulsion of the carbon dioxide by heating, absorption and weighing of the gas in caustic potash. He states "we may assume the same conditions hold good with baryta-water."

The writers have found carbonic acid in calcium hydroxide solutions to range from 0 to 6 or 7 parts per million, although on an average the quantity was less than 3 parts per million. In the case of barium hydroxide solutions we have never found over 1 part per million of carbonic acid, and the average appears to be less than 0.5 part per million. The error arising, therefore, from dissolved carbonates in barium hydroxide solutions, in the absence of other salts which may effect their solution, we are inclined to believe, may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sample being titrated, however, is a source of error which must be carefully avoided. This arises from the direct solution of these salts in the titrating acid; and this is true whether oxalic acid is used or sulphuric acid, which latter was employed by the writers. This is shown by the following experiments:—

Table showing Solubility of Suspended Carbonates by Titrating Acid.

I. Acid added to Alkali.

Solution used.	Containing no suspended carbonates. N/50 sulphuric acid.	Containing suspended carbonates. N/50 sulphuric acid.	Remarks.
C.c.	C.c.	C.c.	
10	3.9	5.0+	End-point indefinite with suspended carbonates.
Solution used.	N/20 (approx.) oxalic acid.	N/20 (approx.) oxalic acid.	
C.c.	C.c.	C.c.	
10	2.2	2.7+	End-point indefinite with suspended carbonates.

On another sample the following results were obtained:—

I. Acid added to Alkali.

Solution used.	Containing no suspended carbonates. N/50 sulphuric acid.	Containing suspended carbonates. N/50 sulphuric acid.	Remarks.
C.c.	C.c.	C.c.	
10	5.0	7.0+	End-point indefinite with suspended carbonates.

II. Alkali added to Acid.

10	5.0	7.0+	End-point indefinite with suspended carbonates.
----	-----	------	---

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for, as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann ("Chem. Analyses des Wassers") admits that duplicate results may vary from 5 to 10 parts per million, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59.2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

Table showing Effect of Ammonium Chloride in holding Carbonates in Solution.

No.	Solution (approx. N/20) barium hydroxide.	Saturated solution ammonium chloride.	Carbonic acid (CO ₂) obtained. Parts per million.
1.	C.c.	C.c.	
	10	0	57.4
2.	45	0	60.0
3.	10	2	0.0 (a)
4.	20	2	0.0 (b)
5.	30	2	46.0
6.	45	2	56.6

(a) In the third experiment no loss of barium hydroxide resulted, and 38.4 parts per million of fixed carbonic acid were indicated in addition.

(b) No loss of barium resulted in the fourth experiment, and 1.9 parts per million of fixed carbonic acid were found in addition.

* *Journal of the American Chemical Society*, xxiii., No. 6.

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 c.c. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough; and such a condition might easily arise in a water containing low amounts of magnesium but considerable carbonic acid, which latter would use up a large proportion of the barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made:—

Table showing Effectiveness of Ammonium Chloride in holding Magnesium Salts in Solution.

Solution of Magnesium Sulphate. Total volume of Solution equal to 150 c.c.			
Barium hydroxide solution (approx. N/20).	Saturated solution ammonium chloride.	Magnesium oxide added.	Magnesium oxide precipitated.
C.c.	C.c.	Parts per million.	Parts per million.
45	0.5	27	2.0
45	0.5	27	1.4
45	0.5	91	9.4
45	2.0	27	0
45	2.0	27	0
45	2.0	91	0

Solution of Magnesium Carbonate (total volume equal to 100 c.c.).

45	2.0	15	0
45	2.0	15	0
45	2.0	15	0

It is evident that 0.5 c.c. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two c.c. are, however, able to hold in solution at least 90 parts per million of the oxide without any of it precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless the precipitation is complete an error is introduced into the correction. The following experiments show that this precipitation is not complete under certain conditions.

Table showing Incomplete Precipitation of Magnesium Hydroxide by Barium Hydroxide.

Solution of Magnesium Carbonate containing 15 parts per Million of Magnesium Oxide. Total volume of Solution equal to 100 c.c.

Barium hydroxide solution.	Magnesium oxide precipitated.	Magnesium oxide not precipitated.
C.c.	Parts per million.	Parts per million.
45	13.7	1.3
45	13.7	1.3
45	12.0	3.0
45	13.7	1.3
45	12.0	3.0
45	12.0	3.0
45	12.0	3.0
Average ..	12.6	2.4

From the above it will be seen that, on an average, 2.4 parts per million of magnesium oxide, equivalent to 2.6 parts per million of carbonic acid, were not precipitated in a solution containing 45 c.c. of an approximately 0.05 normal solution of barium hydroxide in a total volume of 100 c.c. From a large number of experiments made with a standard magnesium sulphate solution, it has been found that the same is true of this salt, *i.e.*, that the magnesium is but partially precipitated under certain conditions.

A large excess of barium hydroxide is necessary in order to effect practically complete precipitation, and unless this excess is maintained as the quantity of magnesium increases, the quantity of magnesium which remains unacted upon will also increase.

This is well shown by the following table, where constantly increasing amounts of magnesium were introduced into the solution.

Table showing Incomplete Precipitation of Magnesium Hydroxide with continually Increasing Amounts of Magnesium Sulphate.

Solution of Magnesium Sulphate. Total Volume of Solution equal to 100 c.c.

Barium hydroxide solution.	Magnesium oxide added.	Magnesium oxide precipitated.	Magnesium oxide not precipitated.
C.c.	Parts per million.	Parts per million.	Parts per million.
45	9.0	10	0
45	27.0	24	3.0
45	54.0	50	4.0
45	91.0	76	15.0

It will be noted that, in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on samples in which the magnesium is in small amount while the barium hydroxide is in large excess. It is due to the fact that the loss of barium hydroxide by carbonating is always greater in such cases.

The error from this cause, which may be called the "error of manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions; the former tending to increase the apparent precipitation, and the latter to decrease it. It is probable, therefore, that the quantity of magnesium oxide not precipitated may be greater than is indicated above.

How seriously this error may affect results is shown by the following table. A standard solution was prepared and was found to contain, by Trillich's method, when no magnesium salts were present, 46.2 parts per million of free and half-bound carbonic acid. This result was the average of ten closely agreeing determinations on this solution; and the figures for the carbonic acid found, when magnesium was present, should be compared with it.

Table showing effect of Non-precipitation of Magnesium Hydroxide in Determinations of Carbonic Acid by Trillich's Method.

MgO added, equiv. to CO ₂ .		Ba(OH) ₂ solution, found by titration.		CO ₂ found by correction for MgO.		Theoretical CO ₂ corrected for MgO.		MgO equiv. to parts per million CO ₂ .	
Parts per million.	C.c.	Parts per million.	Uncorr.	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Pre-precipitated.	Not precipitated.
10	10	49.5	10	39.5	3.3	6.7			
10	10	50.6	10	40.6	4.4	5.6			
10	10	49.4	10	39.4	3.2	6.8			
10	10	49.4	10	39.4	3.2	6.8			
10	10	49.4	10	39.4	3.2	6.8			
20	15	59.2	20	39.2	13.0	7.0			
20	15	57.9	20	37.9	11.7	8.3			
20	15	57.9	20	37.9	11.7	8.3			
20	15	57.9	20	37.9	11.7	8.3			
20	15	57.9	20	37.9	11.7	8.3			
30	15	64.6	30	34.6	18.4	11.6			
30	15	63.4	30	33.4	17.2	12.8			
30	15	64.6	30	34.6	18.4	11.6			
50	20	83.0	50	33.0	36.8	13.2			
50	20	81.6	50	31.6	35.4	14.6			
50	20	83.0	50	33.0	36.8	13.2			

Note.—Amount of magnesium oxide actually present is equal to 10/11 of amounts given as "MgO equivalent to parts per million of CO₂."

The results given above of course exaggerate the error because of the small amount of barium hydroxide and the

large amounts of magnesium. They serve to show, however, the error which might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's methods may be briefly summed up as follows:—
1. The error due to the carbonating of the barium hydroxide as a result of manipulation. This is common to both methods, and tends to make results higher than they should be. With careful work it can be kept very low, and ought not to exceed 1 or 2 parts per million.

2. In Pettenkofer's method the solution of the carbonates by ammonium chloride, which tends to lower the results, seems to be the source of greatest error. The magnitude of this error appears to be governed by the concentration of the barium hydroxide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 c.c. of 0.05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 c.c. of an approximately 0.05 normal barium hydroxide solution is added to each 100 c.c. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralise each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes exceeds the increase, and in consequence too low results are obtained.

(To be continued).

ON THE METEORIC STONES WHICH FELL
NEAR ZOMBA, BRITISH CENTRAL AFRICA,
ON JANUARY 25TH, 1899.
WITH NOTES ON THE CHEMICAL ANALYSIS
OF SUCH BODIES.*

By L. FLETCHER, M.A., F.G.S.,
Keeper of Minerals in the British Museum.

(Concluded from p. 92).

Attracted Material: First Set of Extracts.

40. The $\text{Fe}_2\text{O}_3, \text{P}_2\text{O}_5, \text{SiO}_2$ 0.4933 (§ 2) consists of Fe_2O_3 0.4895 (corresponding to Fe 0.3427), P_2O_5 0.0003 (corresponding to P 0.0001), (SiO_2 0.0028 due to the action on the vessels).

The phosphorus being present as Fe_2NiP (schreibersite) requires Fe 0.0004, Ni 0.0002.

The Ni(Co) due to nickel-iron (§ 2) is thus 0.0487—0.0002 or 0.0485.

Hence we have—

Extracted:—Nickel-iron	{ Fe 0.0342 }	0.3908
	{ Ni(Co) .. 0.0485 }	
Schreibersite		0.0007
Residue (§ 3)		0.3385
Total		0.7300
Weight taken		0.7421

No great stress can be laid on the loss of weight (0.0121), owing to the character of the necessary operations.

The percentage composition of the nickel-iron (0.3908) which has passed into solution is Fe 87.59, Ni(Co) 12.41.

Further, $3\text{K}_2\text{SO}_4.2\text{CoSO}_4$ 0.0166 corresponds to Co 0.0024; hence the percentage composition of the Ni(Co) is Ni 95.07, Co 4.93, and that of the nickel-iron is Fe 87.59, Ni 11.80, Co 0.61, Cu trace.

Attracted Material: Second Set of Extracts.

41. Fe_2O_3 0.0439 (§ 3) corresponds to Fe 0.0307; and the Ni(Co) is 0.0135.

Hence we have—

Extracted:—Nickel-iron	{ Fe 0.0307 }	0.0442
	{ Ni(Co) .. 0.0135 }	
Residue (§ 4)		0.2850
Total		0.3292
Weight taken		0.3366

As before, no stress can be laid on the loss of weight (0.0074); the percentage composition of the nickel-iron (0.0442) extracted in the second series of operations is Fe 69.46, Ni(Co) 30.54.

Attracted Material: Residue.

42. The $\text{Fe}_2\text{O}_3, \text{SiO}_2$ 0.0450 (§ 4) consists of Fe_2O_3 0.0447 (corresponding to Fe 0.0306) and SiO_2 0.0013 (due to the action on the vessels).

$\text{Mg}_2\text{P}_2\text{O}_7$ 0.1137 corresponds to MgO 0.0412 (having regard to the smallness of this amount, the action of the nitric acid on the vessels must likewise have been small, and no deduction is made); the MgO being due to the silicates, other constituents in corresponding proportion must likewise be due thereto; hence the quantities will be (§ 35):— SiO_2 0.0420, MgO 0.0412, FeO 0.0245, MnO 0.0005, CaO 0.0011, making altogether 0.1093 of silicate decomposed by the hydrochloric acid; this leaves SiO_2 0.0027 (namely, 0.0447—0.0420) unallotted; the above quantities are only approximate, for the enstatitic and feldspathic silicates are acted on by the acid and sodic solutions, and their proportions to the olivine are probably different from those which obtain in the unattracted material. Further, FeO 0.0245 of the silicate corresponds to Fe 0.0191, which is included in the above total Fe 0.0306; the Fe due to the alloy itself is thus 0.0115.

Hence we have—

Final residue (enstatite, &c.)	 0.1409 (§ 4)
Silicate decomposed (olivine, &c.)	 0.1093
Fe	 0.0115
Ni(Co)	 0.0072
Unallotted SiO_2	 0.0027
Total	 0.2716
Weight taken	 0.2757

The loss in this case (0.0041) is, partly at least, oxygen; the amount of oxygen necessary to convert the whole of the iron into Fe_3O_4 would be 0.0044. That there is a certain amount of unoxidised metal present is shown by the effervescence of the material with the acid (§ 4); that there is oxide present is indicated by the extreme slowness of action of the mercuric solution on the material (§ 3). As there is only a small proportion of black opaque matter visible in the thin sections when examined with the microscope, and this is probably chromite, the oxidation had probably taken place during the analysis itself, as already suggested (§ 2). The iron and nickel in this residue corresponding to original metal will thus be Fe 0.0115, Ni(Co) 0.0072, corresponding to 0.0187 of alloy having the percentage composition Fe 61.50, Ni(Co) 38.50.

43. Hence we have the following results:—

	Nickel-iron.	Fe.	Ni(Co).	Percentage of Ni(Co).
First extracts	.. 0.3908	0.3423	0.0485	12.41
Second extracts	0.0442	0.0307	0.0135	30.54
Residue	.. 0.0187	0.0115	0.0072	38.50

* From the *Mineralogical Magazine*, vol. xiii., No. 59, 1901.

Hence, of the total nickel-iron contained in the attracted material, 86.13 per cent are removed in the first set of extractions, 9.75 in the second, and the remaining 4.12 is left partly as oxide and partly as metal, the latter protected from the mercuric solution by enclosing oxide or silicate. The variation of the percentage of nickel (cobalt) from 12.41 to 38.50, as the extraction proceeds, does not necessarily imply the existence of different alloys of nickel-iron in the material; it is probably a mere result of the easier oxidation of the iron than the nickel during exposure of the alloy to the atmosphere in the course of the operations.

Attracted Material: Mineral Composition.

44. Calculation, from these numbers, of the composition of the various residues leads to the following composition for the attracted material:—

	Grms.
Nickel-iron	1.2422
Olivine	0.3373
Enstatite	0.3474
Oligoclase	0.0875
	2.0144

for the proportion of the decomposed to the undecomposed silicate is known from § 42, and the proportion of the enstatite to the oligoclase may be taken to be the same as for the previous similar material (§ 28).

Mineral Composition of the Fragment.

45. From §§ 39, 44, the mineral composition of the complete fragment was—

	Grms.	Zomba. Percentages.	Linn County.* Percentages.
Nickel-iron	1.2422	8.61	10.54
Olivine	6.1267	42.44	41.85
Enstatite	5.0238	34.80	
Oligoclase	1.2662	8.77	41.24
Troilite	0.7005	4.85	6.37
Chromite	0.0758	0.53	—
	14.4352	100.00	100.00

Mineralogical Relationship to other Meteoric Stones.

The Zomba meteorite thus consists of a stony material composed of olivine and enstatite in nearly equal quantity admixed with a certain amount of oligoclase; embedded in this stony material are nickel-iron and troilite in considerable quantity and small amounts of chromite and schreibersite. In the aspect of the thin sections as seen under the microscope, in the proportions of the mineral constituents (§ 45), in the percentage composition of the silicate decomposed by hydrochloric acid (§ 36), and in that of the silicate obtained as a residue after the action of the acid and the sodic solution (§ 23), the Zomba meteorite closely resembles the stone which fell in Linn County, Iowa, U.S.A., on February 25th, 1847; different parts of one meteoric stone would generally show greater differences. The composition here assigned to the Zomba enstatite, after analysis of what is interpreted to be a mixture of enstatite and oligoclase, is very near to that found by Professor Tschermak for the coarse grains of enstatite which he was able to isolate from the Lodran stone for chemical determination (§ 27), and the specific gravity as calculated for the Zomba enstatite from the specific gravity of the mixture is virtually identical with the specific gravity directly determined by Professor Tschermak for the isolated Lodran Mineral (§ 29). Further, it is found that the "undecomposed residue," when itself subjected to the treatment used in the analysis of the unattracted material, loses nearly 12 per cent of its weight; the enstatite is chiefly acted upon by the acid, the oligoclase by the sodic solution (§ 30).

THE PREPARATION OF OSMOTIC MEMBRANES
BY ELECTROLYSIS.

By H. N. MORSE and D. W. HORN.

THE difficulties with which Pfeffer had to contend in the preparation of suitable semipermeable membranes for the investigation of osmotic pressure are well known, and need not therefore be rehearsed. Yet, notwithstanding the importance of the subject, no suggestion appears to have been made up to the present time which has helped to obviate any of those difficulties or in any degree to lessen them. The method of Pfeffer has not been improved, and, judging from the testimony of many who have tried it, attempts to prepare the Pfeffer cell usually fail to give satisfactory results.

In this connection, it occurred to the authors that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall, and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall. The results of our experiments in this direction appear to have justified the expectation, and to be worthy of a brief preliminary notice.

The first problem concerned, of course, the effective removal of the air in the walls of the porous cups, since the presence of air obviously interferes with the formation of a sound membrane. For this purpose we have taken advantage of the strong "endosmose" which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the electrodes are immersed. A boiled solution of potassium sulphate containing about 0.5 gm. of the salt in the litre was filled into the porous cup and into the beaker in which it was placed until the level of the liquid within and without reached nearly to the edge of the cup. On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner. As the liquid within the cup rose, it was removed from time to time with a pipette or by means of an intermittent syphon, and replaced by pouring more of the solution into the liquid outside the cup. The quantity of water forced through the wall in this way was considerable. As a rule, we have continued the electrolysis of the sulphate until 300 c.c. had been removed by the pipette or syphon, which required ordinarily about one hour. The cup was then emptied, washed, and placed in a large volume of distilled water until required for the deposition of the membrane.

To form the membrane, the wet cup was placed in a beaker and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with the dynamo so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution (N/10 or N/5 sulphate), and that of the potassium ferrocyanide (also N/10 or N/5), were introduced as nearly simultaneously as possible. At first there is considerable endosmose in the direction of the current, i.e., from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. Both walls remained perfectly clean and free from discolorations except in a few instances, in which, for some reason not yet determined, metallic copper was deposited on the outside of the cup. At the upper edge of the cup, however, nearly midway between the two sides, there soon

* Monatsb. Ak. Wiss. Berlin, 1870, p. 458.

appears a line of reddish-brown colour, showing in general the position of the membrane with respect to the outer and inner walls of the cup. The resistance usually rises quite rapidly, reaching in extreme cases 3000 ohms within an hour, while the endosmose diminishes correspondingly. The most rapid rise in resistance is observed in the less porous hard-burned cups. In the softer and more porous ones, the resistance may not exceed 200 or 300 ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing apparently to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again.

Having obtained the desired resistance, the cell was removed, rinsed inside and out, filled with distilled water, and placed in a beaker containing water, care being taken, of course, not to allow any of the liquid from the inside to come in contact with the outer surface of the cup, and *vice versa*.

Our first experiments were with ordinary porous battery cups holding approximately 250 c.c. On treating some of these in the manner described above until a resistance of from 1500 to 3000 ohms had been reached, they were tested as to the presence of a sound membrane within their walls by filling them one-third full of a normal solution of sugar, and then immersing them in water until the liquids within and without were on the same level. The water entered quite rapidly, and the cups usually began to overflow within from fifty to seventy-five hours. On breaking the cups, the membrane could be seen as a thin line along the fracture surfaces. Ordinarily it was located about midway between the two walls except where the material of the cup manifestly lacked uniformity. In such places the line would bend to one side or the other, and again return to its original direction beyond the uneven spots. The experiment was repeated with the same result with samples of all the various kinds of porous battery cups which had accumulated in the laboratory. It was found that a membrane which would at least exhibit osmotic activity could be made in the walls of any of them without difficulty. It was also tried with certain other cups which had been specially made with a view to the rapid filtration of liquids, and which were, therefore, much more porous than the ordinary battery cup. We could form a membrane in these, but it was necessary to exercise some care in the control of the current. Otherwise the resistance would occasionally drop in a marked degree, indicating a rupture of the membrane. The resistance, in the case of the cups last mentioned, could not be raised above a certain point, which was far below that which could easily be obtained in less porous cups.

With a view to testing the power of the electrolytically prepared membrane to resist pressure, we had made at a local pottery some bottle-shaped cells having a capacity of about 250 c.c. After depositing the membrane in these, in the manner described, they were filled with a normal solution of sugar, closed with rubber stoppers through which glass tubes had been passed, and placed in beakers of water standing upon the floor. Other lengths of tubing were added until the ceiling, 5·5 metres above the floor, was reached. Our tubes began to overflow in periods ranging from six to fifteen hours. When the open manometers were replaced by closed ones containing mercury, the cells failed; not, however, in consequence of ruptured membranes. In manufacturing such vessels, the bottom is made separately, and is inserted and cemented in its place after withdrawing the mould upon which the rest of the bottle is formed. The union between the two parts proved to be a weak one in the case of our cells. Before any considerable pressures were reached the bottoms gave way, permitting the sugar solutions to escape. In most instances the line of detachment could be seen, but not in all. We therefore added a little ferrocyanide to the solutions of sugar, and a little copper sulphate to the water in which the bottles stood in order to ascertain whether

any of the sugar escaped at other places. A reddish-brown circular line then appeared where the two parts had been joined, but nowhere else.

Our next experiments were with small porous cups, such as are employed in making standard battery cells. These were about 85 by 25 m.m., internal measurement, and were provided with a flange at the top. We had found by previous experience that the forcing of a stopper into a cell is liable to injure the membrane, hence we cemented glass tubes in the cups before forming the membranes. In order to make the union more secure, channels were cut on the inside of the cups a little below the rim and parallel to it. The glass tubes, 125 m.m. long, and with external diameters somewhat less than the internal diameters of the cups, were provided with rubber rings at one end, of such thickness that rubber and glass together made moderately tight stoppers for the cups. These were pushed into the cups until the upper edges of the rubber rings were a little below the channels. The spaces above the rubber were then filled with the cement, which was made by mixing 5 parts of litharge with 1 part of glycerin. After hardening for forty-eight hours, the exposed surface of the cement was painted to protect it from liquids, with a solution of equal parts of rubber and paraffin in carbon bisulphide. The cups were then freed from air, and the membranes deposited in the usual manner. When the rubber stoppers carrying the closed manometers were inserted, provision was made for the escape of the superfluous sugar solution by manipulating a small steel rod between the rubber and the glass. The rod was afterwards extracted with a pair of forceps. In the first cell prepared in this way the pressure rose within an hour to 3·25 atmospheres, when the stopper began to give way. It was again crowded into place, and the pressure rose to a little over 3·5 atmospheres, but from this point the stopper was slowly pushed out of the tube. We then emptied the cell and shrunk the end of the glass tube in the flame to about three-fourths its original diameter, in order to give the stopper a more secure hold in the glass. With this modification we were able to secure pressures a little above 4·5 atmospheres. At that pressure, however, the sugar solution always began to ooze out between the manometer and the rubber stopper, and the stopper itself to move upward out of the tube.

We have found it impossible, with the crude manometer hitherto employed by us, to test our membranes at pressures much above 4·5 atmospheres; and it is clear that, to do this, rubber stoppers must be dispensed with, and some suitable metallic connection devised to join the manometer to the cell.

We have made no attempt as yet to measure osmotic pressure, our object at present being only to test the strength of the membranes. It seems improbable that the total osmotic pressure of concentrated solutions, *e.g.* molecular-normal ones, will ever be directly measured. It should, however, be practicable to construct cells in which the pressure of dilute solutions can be quite accurately determined. In that case, it should be feasible to measure the pressures of more concentrated ones by a differential method. For example, having obtained a membrane of such quality in a cell of such construction that the osmotic pressure of a tenth-normal solution can be satisfactorily measured, the pressure of a two-tenths normal solution could be determined by immersing the cell, not in water, but in a one-tenth normal solution, &c. It is probably safe to predict that if a method of determining molecular weights or electrolytic dissociation, by measuring osmotic pressure, is ever worked out, it will be developed along this line. That is, differences of pressure rather than the enormous totals will be measured. It is hoped that the electrolytic method of making semipermeable membranes, when developed by further study, may do away with what has hitherto appeared to be an insurmountable obstacle in the way of progress in this direction.—*American Chemical Journal*, xxvi., No. 1.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A SUMMARY).

By HARRY C. JONES.

(Continued from p. 96).

Inorganic Solvents (continued).

Sulphur Dioxide.—That liquid sulphur dioxide has the power to dissociate salts into their ions is shown by the work of Walden (*Ber. d. Chem. Ges.*, xxii., 2862), on the conductivity of solutions in this solvent. He worked with seven iodides, one bromide, and two sulphocyanates, and measured their conductivities at 0° , in dilutions ranging from a few litres to 100 or 200 litres. A few of his results are given:—

Potassium bromide.		Ammonium iodide.		Potassium sulphocyanate.	
v.	μ v.	v.	μ v.	v.	μ v.
14.6	30.9	20.3	36.3	10.4	17.4
29.4	30.5	30.2	37.6	22.2	17.8
38.6	31.7	54.8	43.5	36.3	19.2
50.2	33.2	91.5	49.2	53.9	20.9
71.5	35.4			73.0	22.9

Walden compared these values with those of the corresponding salts in water at 0° , and found that the conductivities in liquid sulphur dioxide are from one-fourth to one-half the conductivities in water, under the same conditions.

He determined also the molecular weights of a number of salts in liquid sulphur dioxide, by the boiling-point method, and obtained the surprising result that many of the substances which conducted gave abnormally large molecular weights. Some results which are analogous to these were obtained by Franklin and Kraus (*Amer. Chem. Journ.*, xx., 848), in liquid ammonia as the solvent. The probable explanation is that while there is some dissociation into ions, there are also molecular aggregates present of a high degree of complexity. This would account for the facts observed.

Sulphur Dichloride, Sulphuryl Chloride, Thionyl Chloride, Phosphorus Oxychloride, Arsenic Trichloride, Antimony Trichloride.—Walden (*Zeit. Phys. Chem.*, xxv., 209), has quite recently studied the dissociating power of the above-named solvents, and finds that all of them break down electrolytes into their ions to a marked extent. An example or two will suffice:—

Tetraethylammonium iodide in phosphorus oxychloride.		Trimethylsulphine iodide in arsenic trichloride.	
v.	μ v.	v.	μ v.
250	28.91	250	51.44
500	33.45	500	57.90
750	26.11	750	60.75
1500	41.60	1500	66.60

Walden also studied solutions of salts in boron trichloride, phosphorus trichloride, phosphorus tribromide, antimony pentachloride, silicon tetrachloride, stannic chloride, sulphur trioxide, and bromine, and found that these substances have little or no ionising power. Phosphorus trichloride cannot dissociate electrolytes, while phosphorus oxychloride has a strong ionising power; similarly, antimony pentachloride cannot dissociate electrolytes, while the trichloride dissociates to a very considerable extent. We therefore cannot draw any conclusion in reference to the dissociating action of a solvent, knowing the dissociation in solvents which are closely allied to it chemically.

Organic Solvents.

Methyl Alcohol.—When we turn to the organic solvents, we find that considerable work has already been done on the conductivity of electrolytes dissolved in some of them.

This is especially true of methyl and ethyl alcohols. Fitzpatrick (*Phil. Mag.*, xxiv., 378), studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride, and calcium chloride in methyl alcohol, and found values which, though less than in water, were very considerable. Hartwig (*Wied. Ann.*, xxxiii., 58; xliii., 838), measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschkow (Charkow, 1892), studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer (*Wied. Ann.*, lii., 328), worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, for a considerable range of dilution. Holland (*Wied. Ann.*, l., 263), studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium, and ammonium nitrates, and sodium chloride. Carrara (*Gazz. Chim. Ital.*, xxvi., [1], 119), carried out, by far, the most extensive investigation of salts in methyl alcohol which has yet been made. He measured the conductivities of the following substances at various dilutions:—Sodium chloride, iodide, methylate, acetate; lithium chloride, potassium chloride, bromide, iodide, methylate; ammonium chloride, bromide, iodide, and fluoride; tetraethylammonium chloride, bromide and iodide, tetramethylammonium iodide, triethylamine, diisopropylamine, and a number of sulphur derivatives. The conductivities in methyl alcohol of lithium and calcium chlorides, lithium, sodium, and barium bromides, potassium iodide, ammonium nitrate, and potassium acetate were determined by Kerler ("Dissertation, Erlangen," 1894), in Beckmann's laboratory. The conductivity of mercuric iodide in methyl alcohol was measured by Cattaneo (*Rend. R. Acc. Linc. Roma*, 1895); Schall (*Zeit. Phys. Chem.*, xiv., 701), determined the conductivity of hydrochloric, picric, oxalic, and dichloroacetic acids in methyl alcohol; Kablukoff (*Zeit. Phys. Chem.*, iv., 429), also studied the conductivity of hydrochloric acid in methyl alcohol; and Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 26), measured the conductivities of ferric chloride and antimony trichloride in this solvent.

The most satisfactory work, on the whole, which has ever been done on the conductivity of solutions in methyl alcohol, is that of Zelinsky and Krapivin (*Zeit. Phys. Chem.*, xxi., 35). Their work included a number of salts in pure methyl alcohol, as well as in a mixture of methyl alcohol and water, as we shall see later. They used in their work potassium bromide and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethyl-stannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloroacetic acid.

A few of the results obtained by Zelinsky and Krapivin are given below. These suffice to show the relation between the conductivities in methyl alcohol and in water. (See p. 95).

Potassium bromide.		Ammonium iodide.		Hydroxylamine hydrochloride.	
v.	μ v.	v.	μ v.	v.	μ v.
32	69.02	16	72.24	16	54.39
64	76.70	32	78.74	32	62.18
128	83.60	64	85.0	64	69.52
256	88.96	128	91.14	128	75.98
512	93.26	256	96.20	256	81.21
1024	97.25	512	100.6	512	85.15
2048	100.1	1024	104.7	1024	87.30
4096	101.4			2048	85.70

Comparing these values of the molecular conductivity in methyl alcohol with those of potassium chloride at the same dilution in water, we see that they are not very different. The conductivity in methyl alcohol is about two-thirds to three-fourths that in water, under the same conditions.

* *American Chemical Journal*, xxv., No. 3.

An examination of the above results will show that even in as strong a dissociant as methyl alcohol, it is almost impossible to reach the value of μ_{∞} directly by the conductivity method. That dilution at which the salt would be completely dissociated by this solvent is so great that it is impossible to apply the conductivity method to it with any degree of accuracy. It is therefore not possible to measure dissociation accurately, even in methyl alcohol, by the conductivity method.

Another method has been used by Jones (*Zeit. Phys. Chem.*, xxxi., 114), to measure the dissociation of salts by methyl alcohol. He so improved the boiling-point method that it can be used to measure dissociation in a solvent like methyl alcohol to a fair degree of accuracy. The salts used were potassium, sodium, and ammonium bromides; potassium, sodium, and ammonium iodides; potassium and sodium acetates; and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling-point method, is, in round numbers, about two-thirds of that in water under the same conditions.

Ethyl Alcohol.—The number of those who have worked on solutions in ethyl alcohol is quite as large as in methyl alcohol. Fitzpatrick (*Phil. Mag.*, xxiv., 378), measured the conductivities of solutions of calcium chloride, calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig (*Wied. Ann.*, xxxiii., 58; xliii., 838), determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini (*Biebl. Wied. Ann.*, ix., 131), used the following chlorides:—Ammonium, lithium, magnesium, calcium, cadmium, zinc, and cupric; while Cattaneo (*Biebl. Wied. Ann.*, xviii., 219, 365), studied mercuric, ferrous, and ferric chlorides, cadmium bromide, and cadmium iodide. Cattaneo found that these substances have a negative temperature coefficient of conductivity. Völlmer (*Wied. Ann.*, lii., 328), used a larger number of salts in ethyl alcohol than in water. These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium, and calcium chlorides, and calcium and silver nitrates. Kawalki (*Wied. Ann.*, lii., 324), compared the diffusion of a series of salts in water and in ethyl alcohol, and found that the rates of diffusion in the two solvents bore the same relation as the maximum molecular conductivities in these solvents. Reference should be made to the work of Paschkow ("Dissertation," Charkow, 1892), who measured the conductivities in ethyl alcohol of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall (*Zeit. Phys. Chem.*, xiv., 701), who worked with picric, oxalic, and dichloroacetic acids; of Wildermann (*Zeit. Phys. Chem.*, xiv., 267), who studied the conductivities of di- and trichloroacetic acids; of Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 26), whose work in ethyl alcohol included ferric chloride and antimony trichloride; and of Kablukoff (*Zeit. Phys. Chem.*, iv., 429), who measured the conductivity of hydrochloric acid in ethyl alcohol. The results obtained by Kahlenberg and Lincoln for the two chlorides with which they worked are given below:—

Ferric chloride.		Antimony trichloride.	
v.	$\mu v.$	v.	$\mu v.$
2'89	9'91	8'11	4'18
11'57	13'70	32'45	7'94
46'28	15'50	64'91	12'30
195'12	19'33	129'81	18'23
390'24	21'20	259'62	29'43

The dissociation of a number of salts in ethyl alcohol, as in methyl alcohol, has been measured by Jones (*Zeit. Phys. Chem.*, xxxi., 133), using the boiling-point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol to from one-third to one-fourth the extent to which they are dissociated by water at the same dilu-

tion. It should be observed that dissociation as measured by the boiling-point method may not be directly comparable with dissociation as measured by the conductivity method, since the two sets of measurements are made at very different temperatures. It, however, seems very probable, from work which is now in progress in this laboratory, that the temperature coefficient of dissociation is quite small, in which case there should be only a small difference between the results obtained by the two methods.

Propyl and Allyl Alcohols; Isopropyl, Isobutyl, and Isoamyl Alcohols.—The dissociating power of alcohols higher in the series than ethyl alcohol has been determined for only a very few substances. A little work has, however, been done on the conductivity of a few electrolytes in the alcohols mentioned above. Schlamp (*Zeit. Phys. Chem.*, xiv., 272), measured the conductivity in propyl alcohol of solutions of lithium and calcium chloride, sodium iodide, and lithium salicylate, and compared the results with those obtained in ethyl alcohol and in water. The conductivity in propyl alcohol is somewhat less than 0.5 that in ethyl alcohol, under the same conditions of concentration and temperature. Carrara (*Gazz. Chim. Ital.*, xxvii., I., 221), made a few measurements of conductivity in propyl and amyl alcohols, and Hartwig (*Wied. Ann.*, xxxiii., 48; xliii., 838), determined the conductivity of formic, acetic, and butyric acids in amyl alcohol. The conductivity of triethylsulphine iodide in isopropyl alcohol was determined by Carrara (*Gazz. Chim. Ital.*, xxvii., I., 221).

Two substances have been studied in isobutyl alcohol; hydrochloric acid by Kablukoff (*Zeit. Phys. Chem.*, iv., 432), and picric acid by Schall (*Zeit. Phys. Chem.*, xiv., 707). Their results are given below:—

Hydrochloric acid in isobutyl alcohol.		Picric acid in isobutyl alcohol.	
v.	$\mu v.$	v.	$\mu v.$
0'49	2'15	101'6	1'48
2'56	3'08	307'4	1'91
50'33	3'84	511'0	2'20
136'62	3'99	638'0	2'30

Kablukoff (*Zeit. Phys. Chem.*, iv., 429), also worked with solutions of hydrochloric acid in isoamyl alcohol, and obtained the following results:—

Hydrochloric acid in isoamyl alcohol.	
v.	$\mu v.$
3'42	1'79
5'44	1'66
8'93	1'47
14'29	1'42
25'42	1'25

The above results bring out the remarkable fact that the molecular conductivity of hydrochloric acid in isoamyl alcohol decreases with increase in dilution. This is the first time we have encountered such a relation.

Ether.—Very little has thus far been done on the conductivity of ethereal solutions. Cattaneo (*Atti. R. Acc. delle Scienze, Torino*, xxviii., 329; *Rendic. R. Acc. dei Lincei*, [5], ii., 1; sem., 295), has measured the conductivity of ethereal solutions of cadmium iodide, cadmium bromide, ferrous and ferric chlorides, aluminium, mercurous and stannous chlorides, salicylic acid, and hydrochloric acid. The conductivities were determined at temperatures ranging from 10° to 30°, and it was found that the conductivity decreased with rise in temperature—ethereal solutions have a negative temperature coefficient of conductivity. Cattaneo also found that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results obtained by Kablukoff, who found a similar result for

hydrochloric acid in isoamyl alcohol. Indeed, Kablukoff (*Zeit. Phys. Chem.*, iv., 431), found also that the conductivity of hydrochloric acid in ether decreased with the dilution.

Acetone and other Ketones.—The conductivities of a number of salts of the alkalis in acetone were published by Cattaneo (*Rend. R. Acc. dei Lincei*, [5], 40, 2^e sem., 63—75), some five years ago. About the same time a paper appeared by St. v. Laszczynski (*Zeit. Elek. Chem.*, 1895, 55), on the conductivity of solutions of some salts in acetone. A number of salts were included:—Lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara (*Gazz. Chim. Ital.*, xxvii., I, 207); but the following results are taken from the work of von Laszczynski.

Lithium chloride.		Potassium sulphocyanate.		Silver nitrate.	
v.	μ_v .	v.	μ_v .	v.	μ_v .
12.44	4.58	2.04	24.4	143.9	13.3
24.88	6.61	4.08	34.5	287.8	14.7
49.76	9.40	8.16	44.2	575.6	16.5
99.52	12.9	16.32	55.1		
		32.64	66.6		

Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 27), measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride, in acetone; and Dutoit and Aston (*Comptes Rendus*, cxxv., 240), as well as Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), studied a number of solutions in acetone and other ketones. Dutoit and Aston pointed out that those solvents which dissociate to the greatest extent are polymerised, as is shown by the surface-tension method of Ramsay and Shields (*Zeit. Phys. Chem.*, xii., 433). They raise the question as to whether there is not a necessary relation between the polymerisation of the solvent and its dissociating power. To test this they measured the conductivity of salts in a number of solvents. In acetone they used cadmium iodide and sodium salicylate.

In addition to acetone they worked with methylethylketone and methylpropylketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate; in the latter, cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found larger conductivity in the methylethyl- than in the methylpropylketone, but the conductivity in acetone was greater than in methylethylketone. The following data will illustrate these statements:—

	Acetone.	Methylethylketone.	Methylpropylketone.
	μ_v .	μ_v .	μ_v .
CdI ₂ ($v=64$) ..	11.6	5.58	2.13
„ ($v=128$) ..	11.9	5.48	1.55

Dutoit and Aston conclude from their work, together with that of Kablukoff (*Zeit. Phys. Chem.*, xii., 433), that there is a general relation between the polymerisation of the molecules of a solvent and its dissociating power.

The work of Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), confirms that of Dutoit and Aston. They find that the values of μ_v for any electrolyte in different solvents, is a direct function of the amount of polymerisation of the molecules of the solvent, and inversely as the coefficients of viscosity of the solvents.

In connection with their work in acetone as the solvent they make this remarkable statement (*Bull. Soc. Chim.*, 334):—"We have found by the boiling-point method that the following salts in acetone have normal molecular weights: Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate," and these substances in acetone conduct the current. Some results already obtained in this laboratory seem to throw light on this apparent discrepancy.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 6, August 5, 1901.

New Method of Preparation of Aniline and the Analogous Alkalis.—Paul Sabatier and J. B. Senderens.—In several previous researches the authors have shown that free hydrogen, acting at low temperatures in presence of certain finely divided metals, is able to fix itself directly on to various unsaturated organic molecules. This is a general method, which can be applied with advantage to the usual methods for hydrogenation performed by nascent hydrogen (from hydriodic acid in sealed tubes, sodium amalgam and water, iron, zinc or tin, and dilute acids). It is the recently prepared nickel, from reduction of its oxide, that the greatest activity has been found. Reduced cobalt, iron, copper, or platinum in a finely divided state possess analogous powers. The authors find that their method of hydrogenation allows of the transformation of nitrobenzene or analogous nitrated derivatives into aniline or corresponding alkalis.

Vapour-tension of Solutions. Arrhenius's Hypothesis.—A. Ponsot.—Unsuitable for abstraction.

MISCELLANEOUS.

Birkbeck Institution.—A competition for twenty Ravenscroft Entrance Studentships of Two and a-half Guineas each will be held on Tuesday and Wednesday September 17 and 18. These Studentships are open to intending Students, and to Students of the Institution of not more than one year's standing. All Candidates must be between the age of 16 and 25. Names must be given in on or before September 10.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1901, the Chemical Laboratory Fresenius was attended by forty-four Students. Of these, thirty-one were from Germany, two from England, two from Austria, two from Russia, one from Luxemburg, one from Belgium, one from Holland, one from Italy, one from Norway, one from the United States of America, and one from Rhodesia in South Africa. There were three Assistants in the Instruction-Laboratory, and twenty-four in the Versuchsstationen (private laboratories). In the certified staff of teachers there has been no change. To this staff belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. Med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and J. Huber (Architect). The next Winter Term begins on October 15. During the Summer Term, 1901, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), on behalf of trade, manufacture, mining, agriculture, and hygiene.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Phosphorus by Colour in Basic Steel.—Can any reader give me details of process, or give references as to where details may be found?—PHOS.

BENZOL 90 %

Wanted in large quantities, supplied yearly.

Address, "F. N. V. 1462," care of
Rudolf Mosse, Frankfurt-on-Maine.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2180.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Principal for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Principal, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Principal. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin (two papers); English (two papers). Any one of the following Languages or Sciences:—Greek, French, German, Sanskrit, or Arabic; Mathematics (two papers); General Elementary Science (two papers); Elementary Mechanics, Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

The first six candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination will respectively receive an Exhibition or a Prize as follows:—The first of such candidates will receive an Exhibition of £30 per annum for the next two years. The second will receive an Exhibition of £20 per annum for the next two years. The third will receive an Exhibition of £15 per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific and Intermediate

Examinations in Medicine, within three academical years from the time of his passing the Matriculation Examination. The fourth will receive a prize to the value of £10 in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of £5 in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.SC. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year, once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.
Balliol College Laboratory.—D. H. Nagel, H. B. Hartley.

Magdalen College Laboratory.—D. R. Wilson, J. J. Manley.

Queen's College Laboratory.—G. B. Cronshaw, A. F. Walden.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrators—W. Haughton, M.B., and W. C. Ramsden.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced, including Physical Chemistry, second year.

2. *Organic Chemistry*.—General, second year; advanced, third year.

3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of *Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholarships are paid £20 per annum, have free commons, and their chambers and tutorial fees are at half the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING, ARCHITECTURE, AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Lecturer—Herbert Jackson, F.C.S.

Demonstrator—P. H. Kirkaldy, F.C.S.

The Academic Year consists of Three terms. The days fixed for the Admission of New Students in the Academic Year 1901-1902 are October 3, January 16, and April 24.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students

who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor—William Ramsay, LL.D., F.R.S., &c.

Assistants—Morris Travers, D.Sc.; E. C. C. Baly, F.I.C.; and F. G. Donnan, M.A., Ph.D.

The Session is divided into three Terms, as follows:—First Term, from Wednesday, October 2nd, till Friday, December 20th; Second Term, from Tuesday, January 14th, till Wednesday, March 26th; Third Term, from Tuesday, April 22nd, till Saturday, June 14th. Class Examinations begin on June 16th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10., Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Mondays and Wednesdays, at 9, during the session.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (about £80 for two years) will also be competed for in the Session 1901-1902; also the Cloth-worker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D., B.Sc.

Assistants—G. S. Newth, G. T. Morgan, D.Sc., and J. C. Philip, M.A., Ph.D., B.Sc.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of

study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany .. .	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics .. .	2	3
Mine Surveying	10	

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixtieth Session will commence on Tuesday, October 1st, 1901.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S., F.I.C.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S. (Dean); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the

requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 1, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1901-1902, Course A). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and

exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry (vacant). Scholar Assistant, Godfrey Rotter.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 1st, 1901. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Inorganic and Physical Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 27th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, B.Sc., Ph.D.

Demonstrator—E. B. Ludlam, B.Sc.

The session 1901-1902 will begin on October 8. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Elementary and Intermediate Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell-Smith, B.Sc., F.I.C., F.C.S.; A. E. Thomas, B.Sc., F.I.C., F.C.S.; H. A. M. Borland, A.R.C.S.

Demonstrators—F. B. Gatehouse; W. H. Collier (of the University of London).

Assistant in Chemical Laboratory—C. E. Young.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical

Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 30th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., F.R.S.

Assistant Lecturer—T. S. Price, Ph.D., D.Sc.

Demonstrator—R. C. Farmer, Ph.D., M.Sc.

Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 1st, 1901.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. At least one of the above meetings of the class in each week will be devoted to tutorial work. Attendance at this tutorial class is compulsory, as is the performance of the weekly exercises set by the Professor. Mondays to Fridays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—**Advanced Organic Chemistry.**—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring

terms. Fee, £2 2s. *General and Physical Chemistry*.—This course will deal in outline with various Chemical subjects. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General, Physical, and Organic Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms ..	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—A. W. Gilbody, Ph.D. (Munich), M.Sc. (Victoria); and S. F. Stell, F.C.S.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—W. J. Willis.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

1. *General Chemistry Course*, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Dyeing*. Extending over one or two years.

V. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VI. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

**ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER.**

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

**VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.**

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.R.S.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D.

Assistant Lecturers and Demonstrators—T. S. Patterson,

Ph.D.; J. McCrae, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrator—H. T. Calvert, B.Sc., Ph.D.

The Session begins October, 1901.

Lecture Courses.

1. *General Course of Chemistry*.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. *Advanced Inorganic Chemistry*.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. *Advanced Inorganic Chemistry*.—Non-metals. Tuesday and Thursday at 9.30 a.m. Fee, £3 13s. 6d.

4. *Organic Chemistry*.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. *Honours Courses*—

(a) *Organic Chemistry*.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

(b) *History of Chemistry*.—Monday and Wednesday at 9.30 a.m. in the First Term. Fee, £1 1s.

(c) *Physical Chemistry*.—Tuesday and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 2s.

(d) *Selected subjects*.—Thursday at 9.30 a.m. in the Second and Third Terms. Fee, £1 1s.

(e) *Electro-chemistry*.—One hour weekly. Fee, £1 11s. 6d.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—T. L. Bailey, Ph.D.; A. N. Meldrum, B.Sc.; A. T. de Moulipied, B.Sc., Ph.D.; and A. W. Titherley, D.Sc., Ph.D.

Assistant—H. H. Froydell.

The Session commences October 3rd.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class.

Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry, with Practical Work. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electro-chemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories recently erected provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, and a Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day . . .	£4	£7
Two days . . .	5 10s.	10
Three days . . .	7	13
Whole week . . .	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C. on Organic Chemistry, Lecture Course D or E, Technological Chemis-

try, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1902, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Principal not later than November 15, 1902. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—J. A. Smythe, B.Sc., Ph.D., and H. W. Cousins, B.Sc.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 10th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 8th. The class for Inorganic Chemistry meets at 9.15 a.m. on Wednesdays, commencing October 9th. Fee for Session,

£3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the second year in an examination in a more advanced stage in any two of these subjects. Associates in Science are admissible one year after obtaining the title of Associate to the examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 30th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University.

OWENS COLLEGE,
VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; and F. V. Darbishire, B.A., Ph.D.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—Dr. Bone.

The Session begins on October 1, 1901.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

METALLURGY.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: The Metallurgical Laboratory will be open to students every day.

ELECTRO-CHEMISTRY.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. Courses of lectures and laboratory instruction will be given to Advanced Chemical Students in the coming Session. *Lecturer*—R. S. Hutton, B.Sc.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical

Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

ELECTRO-CHEMICAL LABORATORY.

In the new Physical laboratories, arrangements have been made for a complete equipment for Electro-chemical and Electro-metallurgical work. Professor of Physics and Director of Physical Laboratories, Arthur Schuster, Ph.D., F.R.S.; Professor T. H. Core, M.A. (Edin.). Lecturer and Assistant Director of Laboratories, Charles H. Lees, D.Sc. (Vict.). Demonstrator and Assistant Lecturer in Electro-technics, Robert Beattie, B.Sc. (Durham). Demonstrator and Assistant Lecturer in Electro-chemistry, R. S. Hutton, M.Sc. (Vict.). Assistant Demonstrators, James Lord, B.Sc. (Vict.); R. C. Wale, B.Sc. (Vict.).

For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, B.Sc., F.I.C.; G. D. Lander, D.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 7th. Evening Classes begin September 23rd.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term,

Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on Electro-chemistry and other special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Pharmacy, Materia Medica, and all other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

Demonstrator—T. Slater Price, D.Sc.

The Session will commence on October 2nd.

Beginners' Course.—Inorganic Chemistry: Thursday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Tuesday and Friday 10 to 11. Fee, £2 2s.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, M.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 18th, and ends on March 19th. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—W. B. Davidson, M.A., D.Sc., and W. Maitland, B.Sc.

I. *General Lecture Course (100 Lectures)*.—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £3 3s.; for subsequent attendance, £2 2s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry (50 Lectures)*.—Daily during the Summer Session. Fee, £2 2s.

III. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. W. B. Davidson. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants—W. W. Taylor, M.A., D.Sc., J. P. Longstaff, B.Sc., and James Kerr, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee, £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee, £1 1s.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the

following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Archibald Boon, B.Sc.; Andrew F. King, F.I.C.; and P. Longstaff, B.Sc.

The Session begins September 30th, 1901.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the third year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1901-1902 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 9th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on

September 27th and following days. Twenty-six of these Bursaries are restricted to Men and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. One Scholarship in Chemistry of the value of £80, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1901-1902.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Second B.Sc. Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—Laboratory Pupils.—The Chemical Laboratory

is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session begins on October 15th, 1901, and ends on June 14th, 1902. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 6th, 1902, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—William Goodwin, F.C.S.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. **Faculty of Medicine.**—First year's Course, Inorganic and Elementary Organic Chemistry. **School of Engineering.**—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. **Faculty of Medicine.**—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. **School of Engineering.**—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commission for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the second time to a Chemistry Student of this College.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—J. Holms Pollok, B.Sc.

Demonstrator of Chemistry and Assaying—A. E. B. Manders.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological

Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 17th, and the Winter Session opens on Tuesday, October 1st. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 17th. Session begins October 1st. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, F.C.S., &c. Session commences Sept. 30.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vit.), assisted by Mr. John L. White, M.Sc., Mr. H. G. Wayling, B.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects. Session opens Sept. 16. The principal work of the Institute is the provision of Evening Classes for both sexes in all subjects of Technology, Pure and Applied Science, Art, Commerce, Domestic Economy, and Music; but it also provides a Technical Day School, a Science Day School for Boys and Girls, a Training School of Domestic Economy, a Domestic Economy School for Girls, a Day School of Art, and Special Day Courses in Science and Technical subjects. During the last Session, 250 Evening Classes in more than 100 different subjects were attended by over 3100 individual students, while 520 students were in regular attendance at the Day Schools and Classes.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, Breams Buildings, Chancery Lane.—Chemistry Courses will be conducted, commencing Monday, September 30, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., D.Sc. This Institution, which has now completed seventy-eight years of educational work in the metropolis, commences its new Session on Monday, September 30th. The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 70 students passed some university examination, while large numbers gained successes at various public examinations. The Institution has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are now very thoroughly equipped. The Day classes provide courses in Chemistry, Biology, Physics, Mathematics, and Geology for the Science Degrees of London University. There are also Day classes in modern Languages, including Russian and Spanish; courses of Lectures on French and German Literature are given both in the afternoon and evening, and also a University Extension course on *Dante* and Italian Literature is arranged for the afternoon. The School of Art is open both day and evening. A new reading room, and a new magazine room have recently been provided. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes and full information about the Institution. A popular Lecture or Entertainment is given in the Theatre every Wednesday evening.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic, Organic, and Electro-Chemistry (Session fees, per course, 8s. to 20s.), Dr. F. Mollwo Perkin, assisted by Dr. E. C. Jee. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 8s. to 10s.), Dr. J. Henderson. Special Evening Courses on Oils and Fats, including Soap and Candle Manufacture, and on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 23, 1901.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 12, Knowle Road, Brixton, London.—Principal, Dr. A. B. Griffiths, F.R.S. (Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with the best appliances. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Professor of Chemistry, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry, including Metallurgy, Oils and Colours, Photography, &c. Special Classes are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 2½d.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Arthur Lapworth, D.Sc. (Lond.), F.I.C.; Assistants, Mr. S. J. Peachey and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 23.

EAST LONDON TECHNICAL COLLEGE, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are conducted in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London. The Day College opens on Sept. 9. Evening Classes begin Sept. 24.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Head of Chemical Department, Mr. H. Charles L. Bloxam. Assistants, Mr. W. H. Watson, A.R.C.S., Mr. E. A. Jenkinson, A.R.C.S. Lectures and Practical Classes in Elementary, Advanced, and Honours Inorganic and Organic Chemistry are held in the evenings from 6.30 or 7 p.m. to 9.30 p.m., affording instruction in the Courses for the Examinations of the University of London and the Board of Education. The Classes form a Course of Study extending over five Sessions, and are open to both sexes. The Laboratories are open to those wishing to pursue investigations. A reference library is attached to the Chemical Department. Session begins September 23.

NORTHAMPTON INSTITUTE (City Polytechnic), St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Lecturers in Technical Chemistry: Mr. C. J. Head, F.I.C., &c.; Mr. S. Field, A.R.C.S.; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping and Stereotyping, and Gold and Silver Assaying. (For full details see Prospectus).

CARPENTERS' COMPANY TECHNICAL INSTITUTE, Jupp Road, Stratford, E.—Principal, William Ping, F.C.S. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *via* the Institute of Chemistry Examination. Students attending the College visit technical works.

WEST HAM MUNICIPAL INSTITUTE.—Principal, Albert E. Briscoe, B.Sc. (Lond.), &c. Chemical Department, Harold A. Auden, M.Sc., &c., assisted by F. H. Streatfeild and H. V. Capey. Day and Evening Classes, commencing September 21.

SOUTH-EASTERN AGRICULTURAL COLLEGE, Wye, Kent.—Chemistry: Professor, A. D. Hall, M.A.(Oxon.); Lecturer, E. J. Russell, B.Sc. (Lond.). Next Session begins October 1. The courses of instruction in Chemistry are suitable to students intending to become analysts or assistants in works manufacturing manures, feeding-stuffs, &c. The College possesses new and well-equipped Laboratories for Chemistry, Botany, and Bacteriology. The farm, gardens, and experiment grounds afford material for investigation and research. Fee: £8 6s. 8d. per term admits to all Lecture Courses, &c.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Mr. W. H. Duckworth, F.C.S., and Mr. H. G. Thompson. Session opens Monday, September 9. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d.).

STOREY INSTITUTE, LANCASTER.—Principal, Wm. French, M.A., F.I.C. Lecturer in Physics, F. E. Rees, B.Sc. Courses arranged in Chemistry and Physics to suit students for B.Sc., &c.

LEEDS TECHNICAL SCHOOL (in connection with the Leeds Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 31 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, A.R.C.S., and Mr. T. R. White, B.A.; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 2s. 6d. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at reduced composition fees. Session commenced Sept. 16th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (163 pp.) post free 4d.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—The new School now in course of completion will be opened in September, 1901. In addition to the ample arrangements provided for Industrial Chemistry, the Committee have decided upon the erection of new building, 1248 square yards in area, for Bleaching, Dyeing, Printing, and Finishing Textile Goods. The new School, it is stated, will be the largest and probably the most completely equipped school in the kingdom.

INSTITUTE OF PUBLIC HEALTH AND TECHNOLOGY, Seymour House, Old Trafford, Manchester.—Principals, Charles Estcourt, F.I.C., F.C.S., &c., and Philip Anderson Estcourt, Ph.D. The course of instruction is especially intended for those who require a knowledge of Chemistry and Bacteriology bearing upon Sanitary matters. Chemical Technology is specially taught with a view to enable Medical Men and others engaged in Sanitary matters to understand the operations at the various works which may come under their control. Persons who desire to take up the branch of Chemical Engineering, including Electrical Engineering, will also have special opportunities of pursuing such studies.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, J. Paul de Castro, M.A. (Cantab.), A.I.C., F.C.S., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, and Blow-pipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar. Session commences Monday, September 11.

TECHNICAL INSTITUTE, SALFORD.—Principal, W. Wilson, M.A. Session begins September 11th. Special attention is directed to the Dyeing and Calico Printing Laboratories. Day and Evening Classes in Science subjects. Also School of Art. Particulars free from Secretary.

WOLVERHAMPTON FREE LIBRARY SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Mr. H. J. Tench; Botany, Mr. Sidney Phillips, Ph.C.; Latin, Mr. F. G. Griffiths, M.P.S. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, Latin, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. The School is recognised by the Examining Board of the Royal College of Surgeons and Physicians, as a centre for preparation in Chemistry and Physics. Session commences Monday, Sept. 9th. For other particulars and programme, apply Mr. J. Elliot, Secretary.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2181.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

GLASGOW, 1901.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. ARTHUR W. RÜCKER, M.A., LL.D., D.Sc.,
Sec.R.S.

THE first thought in the minds of all of us to-night is that since we met last year the great Queen, in whose reign nearly all the meetings of the British Association have been held, has passed to her rest.

To Sovereigns most honours and dignities come as of right; but for some of them is reserved the supreme honour of an old age softened by the love and benedictions of millions; of a path to the grave, not only magnificent, but watered by the tears both of their nearest and dearest, and of those who, at the most, have only seen them from afar.

This honour Queen Victoria won. All the world knows by what great abilities, by what patient labour, by what infinite tact and kindness, the late Queen gained both the respect of the rulers of nations and the affection of her own subjects.

Her reign, glorious in many respects, was remarkable, outside these islands, for the growth of the Empire; within and without them, for the drawing nearer of the Crown and the people in mutual trust; while, during her lifetime, the developments of science and of scientific industry have altered the habits and the thoughts of the whole civilised world.

The representatives of science have already expressed in more formal ways their sorrow at the death of Queen Victoria, and the loyalty and confident hope for the future with which they welcome the accession of King Edward. But none the less, I feel sure that at this, the first meeting of the British Association held in his reign, I am only expressing the universal opinion of all our members when I say that no group of the King's subjects trusts more implicitly than we do in the ability, skill, and judgment which His Majesty has already shown in the exercise of the powers and duties of his august office; that none sympathise more deeply with the sorrows which two great nations have shared with their Sovereigns; and that none cry with more fervour, "Long live the King!"

But this Meeting of the British Association is not only remarkable as being the first in a new reign. It is also the first in a new century. It is held in Glasgow at a time when your International Exhibition has in a special sense attracted the attention of the world to your city, and when the recent celebration of the ninth jubilee of your University has shown how deeply the prosperity of the present is rooted in the past. What wonder, then, if I take the Chair to which you have called me with some misgivings? Born and bred in the South, I am to preside over a Meeting held in the largest city of Scotland. As your chosen mouthpiece I am to speak to you of science when we stand at the parting of the centuries, and when the achievements of the past and present, and the promise of the future, demand an interpreter with gifts of knowledge and divination to which I cannot pretend. Lastly, I am President of the British Association as a disciple in the home of the master, as a physicist in a city which a physicist has made for ever famous. Whatever the future may have in store for Glasgow, whether your enterprise is still to add wharf to wharf, factory to factory, and street

to street, or whether some unforeseen "tide in the affairs of men" is to sweep energy and success elsewhere, fifty-three years in the history of your city will never be forgotten while civilisation lasts.

More than half a century ago, a mere lad was the first to compel the British Association to listen to the teaching of Joule, and to accept the law of the conservation of energy. Now, alike in the most difficult mathematics and in the conception of the most ingenious apparatus, in the daring of his speculations and in the soundness of his engineering, William Thomson, Lord Kelvin, is regarded as a leader by the science and industry of the whole world.

It is the less necessary to dwell at length upon all that he has done, for Lord Kelvin has not been without honour in his own country. Many of us, who meet here to-night, met last in Glasgow when the University and City had invited representatives of all nations to celebrate the Jubilee of his professorship. For those two or three days learning was surrounded with a pomp seldom to be seen outside a palace. The strange middle-age costumes of all the chief Universities of the world were jostling here, the outward signs that those who were themselves distinguished in the study of Nature had gathered to do honour to one of the most distinguished of them all.

Lord Kelvin's achievements were then described in addresses in every tongue, and therefore I will only remind you that we, assembled here to-night, owe him a heavy debt of gratitude; for the fact that the British Association enters on the twentieth century conscious of a work to do and of a vigour to do it is largely due to his constant presence at its Meetings, and to the support he has so ungrudgingly given. We have learned to know not only the work of our great leader, but the man himself; and I count myself happy because in his life-long home, under the walls of the University he served so well, and at a Meeting of the Association which his genius has so often illuminated, I am allowed, as your President, to assure him in your name of the admiration, respect, nay, of the affection, in which we all hold him.

I have already mentioned a number of circumstances which make our Meeting this year noteworthy; to these I must add that for the first time we have a Section for Education, and the importance of this new departure, due largely to the energy of Professor Armstrong, is emphasised by the fact that the Chair of that Section will be occupied by the Vice-President of the Committee of Council on Education—Sir John Gorst. I will not attempt to forecast the proceedings of the new Section. Education is passing through a transitional stage. The recent debates in Parliament; the great gifts of Mr. Carnegie; the discussion as to University organisation in the North of England; the reconstitution of the University of London; the increasing importance attached to the application of knowledge both to the investigation of Nature and to the purposes of industry, are all evidence of the growing conviction that without advance in education we cannot retain our position among the nations of the world. If the British Association can provide a platform on which these matters may be discussed in a scientific but practical spirit, free from the misrepresentations of the hustings and the exaggerations of the partisan, it will contribute in no slight measure to the national welfare.

But amid the old and new activities of our meeting the undertone of sadness, which is never absent from such gatherings, will be painfully apparent to many of us at Glasgow. The life-work of Professor Tait has ended amid the gloom of the war-cloud. A bullet, fired thousands of miles away, struck him to the heart, so that in their deaths the father and the brave son, whom he loved so well, were not long divided. Within the last year, too, America has lost Rowland; Viriamu Jones, who did yeoman's service for education and for science, has succumbed to a long and painful illness; and one who last year at Bradford seconded the proposal that I should be your President at Glasgow, and who would have unquestionably have occupied this Chair before long had he been spared to do so, has

unexpectedly been called away. A few months ago we had no reason to doubt that George Francis FitzGerald had many years of health and work before him. He had gained in a remarkable way not only the admiration of the scientific world, but the affection of his friends, and we shall miss sadly one whom we all cared for, and who, we hoped, might yet add largely to the achievements which had made him famous.

The Science of the Nineteenth Century.

Turning from these sad thoughts to the retrospect of the century which has so lately ended, I have found it to be impossible to free myself from the influence of the moment, and to avoid, even if it were desirable to avoid, the inclination to look backward from the standpoint of to-day.

Two years ago Sir Michael Foster dealt with the work of the century as a whole. Last year Sir William Turner discussed in greater detail the growth of a single branch of science. A third and humbler task remains, viz., to fix our attention on some of the hypotheses and assumptions on which the fabric of modern theoretical science has been built, and to inquire whether the foundations have been so "well and truly" laid that they may be trusted to sustain the mighty superstructure which is being raised upon them.

The moment is opportune. The three chief conceptions which for many years have dominated physical as distinct from biological science have been the theories of the existence of atoms, of the mechanical nature of heat, and of the existence of the ether.

Dalton's atomic theory was first given to the world by a Glasgow professor—Thomas Thomson—in the year 1807, Dalton having communicated it to him in 1804. Rumford's and Davy's experiments on the nature of heat were published in 1798 and 1799 respectively; and the celebrated Bakerian Lecture, in which Thomas Young established the undulatory theory by explaining the interference of light, appeared in the *Philosophical Transactions* in 1801. The keynotes of the physical science of the nineteenth century were thus struck, as the century began, by four of our fellow-countrymen, one of whom—Sir Benjamin Thompson, Count Rumford—preferred exile from the land of his birth to the loss of his birthright as a British citizen.

Doubts as to Scientific Theories.

It is well known that of late doubts have arisen as to whether the atomic theory, with which the mechanical theory of heat is closely bound up, and the theory of the existence of an ether have not served their purpose, and whether the time has not come to re-consider them.

The facts that Professor Poincaré, addressing a congress of physicists in Paris, and Professor Poynting, addressing the Physical Section of the Association, have recently discussed the true meaning of our scientific methods of interpretation; that Dr. James Ward has lately delivered an attack of great power on many positions which eminent scientific men have occupied; and that the approaching end of the nineteenth century led Professor Hæckel to define in a more popular manner his own very definite views as to the solution of the "Riddle of the Universe," are perhaps a sufficient justification of an attempt to lay before you the difficulties which surround some of these questions.

To keep the discussion within reasonable limits I shall illustrate the principles under review by means of the atomic theory, with comparatively little reference to the ether, and we may also at first confine our attention to inanimate objects.

The Construction of a Model of Nature.

A natural philosopher, to use the old phrase, even if only possessed of the most superficial knowledge, would attempt to bring some order into the results of his observation of Nature by grouping together statements with

regard to phenomena which are obviously related. The aim of modern science goes far beyond this. It not only shows that many phenomena are related which at first sight have little or nothing in common, but, in so doing, also attempts to explain the relationship.

Without spending time on a discussion of the meaning of the word "explanation," it is sufficient to say that our efforts to establish relationships between phenomena often take the form of attempting to prove that, if a limited number of assumptions are granted as to the constitution of matter, or as to the existence of quasi-material entities, such as caloric, electricity, and the ether, a wide range of observed facts falls into order as a necessary consequence of the assumptions. The question at issue is whether the hypotheses which are at the base of the scientific theories now most generally accepted are to be regarded as accurate descriptions of the constitution of the universe around us, or merely as convenient fictions.

Convenient fictions be it observed, for even if they are fictions they are not useless. From the practical point of view it is a matter of secondary importance whether our theories and assumptions are correct, if only they guide us to results which are in accord with facts. The whole fabric of scientific theory may be regarded merely as a gigantic "aid to memory"; as a means for producing apparent order out of disorder by codifying the observed facts and laws in accordance with an artificial system, and thus arranging our knowledge under a comparatively small number of heads. The simplification introduced by a scheme which, however imperfect it may be, enables us to argue from a few first principles, makes theories of practical use. By means of them we can foresee the results of combinations of causes which would otherwise elude us. We can predict future events, and can even attempt to argue back from the present to the unknown past.

But it is possible that these advantages might be attained by means of axioms, assumptions, and theories based on very false ideas. A person who thought that a river was really a streak of blue paint might learn as much about its direction from a map as one who knew it as it is. It is thus conceivable that we might be able, not indeed to construct, but to imagine, something more than a mere map or diagram, something which might even be called a working model of inanimate objects, which was nevertheless very unlike the realities of nature. Of course, the agreement between the action of the model and the behaviour of the things it was designed to represent would probably be imperfect, unless the one were a facsimile of the other; but it is conceivable that the correlation of natural phenomena could be imitated, with a large measure of success, by means of an imaginary machine, which shared with a map or diagram the characteristic that it was in many ways unlike the things it represented, but might be compared to a model in that the behaviour of the things represented could be predicted from that of the corresponding parts of the machine.

We might even go a step further. If the laws of the working of the model could be expressed by abstractions, as, for example, by mathematical formulæ, then, when the formulæ were obtained, the model might be discarded, as probably unlike that which it was made to imitate, as a mere aid in the construction of equations, to be thrown aside when the perfect structure of mathematical symbols was erected.

If this course were adopted we should have given up the attempt to know more of the nature of the objects which surround us than can be gained by direct observation, but might nevertheless have learned how these objects would behave under given circumstances.

We should have abandoned the hope of a physical explanation of the properties of inanimate Nature, but should have secured a mathematical description of her operations.

There is no doubt that this is the easiest path to follow. Criticism is avoided if we admit from the first that we

cannot go below the surface; cannot know anything about the constitution of material bodies; but must be content with formulating a description of their behaviour by means of laws of Nature expressed by equations.

But if this is to be the end of the study of Nature, it is evident that the construction of the model is not an essential part of the process. The model is used merely as an aid to thinking; and if the relations of phenomena can be investigated without it, so much the better. The highest form of theory—it may be said—the widest kind of generalisation, is that which has given up the attempt to form clear mental pictures of the constitution of matter, which expresses the facts and the laws by language and symbols which lead to results that are true, whatever be our view as to the real nature of the objects with which we deal. From this point of view the atomic theory becomes not so much false as unnecessary; it may be regarded as an attempt to give an unnatural precision to ideas which are and must be vague.

Thus, when Rumford found that the mere friction of metals produced heat in unlimited quantity, and argued that heat was therefore a mode of motion, he formed a clear mental picture of what he believed to be occurring. But his experiments may be quoted as proving only that energy can be supplied to a body in indefinite quantity, and when supplied by doing work against friction it appears in the form of heat.

By using this phraseology we exchange a vivid conception of moving atoms for a colourless statement as to heat energy, the real nature of which we do not attempt to define; and methods which thus evade the problem of the nature of the things which the symbols in our equations represent have been prosecuted with striking success, at all events within the range of a limited class of phenomena. A great school of chemists, building upon the thermodynamics of Willard Gibbs and the intuition of Van t'Hoff, have shown with wonderful skill that, if a sufficient number of the data of experiment are assumed, it is possible, by the aid of thermodynamics, to trace the form of the relations between many physical and chemical phenomena without the help of the atomic theory.

But this method deals only with matter as our coarse senses know it; it does not pretend to penetrate beneath the surface.

It is therefore with the greatest respect for its authors, and with a full recognition of the enormous power of the weapons employed, that I venture to assert that the exposition of such a system of tactics cannot be regarded as the last word of science in the struggle for the truth.

Whether we grapple with them, or whether we shirk them; however much or however little we can accomplish without answering them, the questions still force themselves upon us:—Is matter what it seems to be? Is interplanetary space full or empty? Can we argue back from the direct impressions of our senses to things which we cannot directly perceive; from the phenomena displayed by matter to the constitution of matter itself?

It is these questions which we are discussing to-night, and we may therefore, as far as the present address is concerned, put aside, once for all, methods of scientific exposition in which an attempt to form a mental picture of the constitution of matter is practically abandoned, and devote ourselves to the inquiries whether the effort to form such a picture is legitimate, and whether we have any reason to believe that the sketch which science has already drawn is to some extent a copy, and not a mere diagram, of the truth.

Successive Steps in the Analysis of Matter.

In dealing, then, with the question of the constitution of matter and the possibility of representing it accurately, we may grant at once that the ultimate nature of things is, and must remain, unknown; but it does not follow that immediately below the complexities of the superficial phenomena which affect our senses there may not be a

simpler machinery of the existence of which we can obtain evidence, indirect indeed but conclusive.

The fact that the apparent unity which we call the atmosphere can be resolved into a number of different gases is admitted; though the ultimate nature of oxygen, nitrogen, argon, carbonic acid, and water vapour is as unintelligible as that of air as a whole, so that the analysis of air may be said to have substituted many incomprehensibles for one.

Nobody, however, looks at the question from this point of view. It is recognised that an investigation into the proximate constitution of things may be useful and successful, even if their ultimate nature is beyond our ken.

Nor need the analysis stop at the first step. Water vapour and carbonic acid, themselves constituents of the atmosphere, are in turn resolved into their elements, hydrogen, oxygen, and carbon, which, without a formal discussion of the criteria of reality, we may safely say are as real as air itself.

Now, at what point must this analysis stop if we are to avoid crossing the boundary between fact and fiction? Is there any fundamental difference between resolving air into a mixture of gases, and resolving an elementary gas into a mixture of atoms and ether?

There are those who cry halt! at the point at which we divide a gas into molecules, and their first objection seems to be that molecules and atoms cannot be directly perceived, cannot be seen or handled, and are mere conceptions, which have their uses, but cannot be regarded as realities.

It is easiest to reply to this objection by an illustration.

The rings of Saturn appear to be continuous masses separated by circular rifts. This is the phenomenon which is observed through a telescope. By no known means can we ever approach or handle the rings; yet everybody who understands the evidence now believes that they are not what they appear to be, but consist of minute moonlets, closely packed indeed, but separate the one from the other.

In the first place Maxwell proved mathematically that if a Saturnian ring were a continuous solid or fluid mass it would be unstable, and would necessarily break into fragments. In the next place, if it were possible for the ring to revolve like a solid body, the inmost parts would move slowest, while a satellite moves faster the nearer it is to a planet. Now spectroscopic observation, based on the beautiful method of Sir W. Huggins, shows not only that the inner portions of the ring move the more rapidly, but that the actual velocities of the outer and inner edges are in close accord with the theoretical velocities of satellites at like distances from the planet.

This and a hundred similar cases prove that it is possible to obtain convincing evidence of the constitution of bodies between whose separate parts we cannot directly distinguish, and I take it that a physicist who believes in the reality of atoms thinks that he has as good reason for dividing an apparently continuous gas into molecules as he has for dividing the apparently continuous Saturnian rings into satellites. If he is wrong it is not the fact that molecules and satellites alike cannot be handled, and cannot be seen as individuals, that constitutes the difference between the two cases.

It may, however, be urged that atoms and the ether are alleged to have properties different from those of matter in bulk, of which alone our senses take direct cognisance, and that therefore it is impossible to prove their existence by evidence of the same cogency as that which may prove the existence of a newly discovered variety of matter or of a portion of matter too small or too distant to be seen.

This point is so important that it requires full discussion, but in dealing with it, it is necessary to distinguish carefully between the validity of the arguments which support the earlier and more fundamental propositions of the theory; and the evidence brought forward to justify mere speculative applications of its doctrines which might

be abandoned without discarding the theory itself. The proof of theory must be carried out step by step.

The first step is concerned wholly with some of the most general properties of matter, and consists in the proof that those properties are either absolutely unintelligible, or that, in the case of matter of all kinds, we are subject to an illusion similar to that the results of which we admit in the case of Saturn's rings, clouds, smoke, and a number of similar instances. The believer in the atomic theory asserts that matter exists in a particular state; that it consists of parts which are separate and distinct the one from the other, and as such are capable of independent movements.

Up to this point no question arises as to whether the separate parts are, like grains of sand, mere fragments of matter; or whether, though they are the bricks of which matter is built, they have, as individuals, properties different from those of masses of matter large enough to be directly perceived. If they are mere fragments of ordinary matter, they cannot be used as aids in explaining those qualities of matter which they themselves share.

We cannot explain things by the things themselves. If it be true that the properties of matter are the product of an underlying machinery, that machinery cannot itself have the properties which it produces, and must, to that extent at all events, differ from matter in bulk as it is directly presented to the senses.

If, however, we can succeed in showing that if the separate parts have a limited number of properties (different, it may be, from those of matter in bulk), the many and complicated properties of matter can, to a considerable extent, be explained as consequences of the constitution of these separate parts; we shall have succeeded in establishing, with regard to quantitative properties, a simplification similar to that which the chemist has established with regard to varieties of matter. The many will have been reduced to the few.

The proofs of the physical reality of the entities discovered by means of the two analyses must necessarily be different. The chemist can actually produce the elementary constituents into which he has resolved a compound mass. No physicist or chemist can produce a single atom separated from all its fellows, and show that it possesses the elementary qualities he assigns to it. The cogency of the evidence for any suggested constitution of atoms must vary with the number of facts which the hypothesis that they possess that constitution explains.

Let us take, then, two steps in their proper order, and inquire, first, whether there is valid ground for believing that all matter is made up of discrete parts; and, secondly, whether we can have any knowledge of the constitution or properties which those parts possess.

The Coarse-grainedness of Matter.

Matter in bulk appears to be continuous. Such substances as water or air appear to the ordinary observer to be perfectly uniform in all their properties and qualities, in all their parts.

The hasty conclusion that these bodies are really uniform is, nevertheless, unthinkable.

In the first place the phenomena of diffusion afford conclusive proof that matter when apparently quiescent is in fact in a state of internal commotion. I need not recapitulate the familiar evidence to prove that gases and many liquids when placed in communication interpenetrate or diffuse into each other; or that air, in contact with a surface of water, gradually becomes laden with water-vapour, while the atmospheric gases in turn mingle with the water. Such phenomena are not exhibited by liquids and gases alone, nor by solids at high temperatures only. Sir W. Roberts-Austen has placed pieces of gold and lead in contact at a temperature of 18° C. After four years the gold had travelled into the lead to such an extent that not only were the two metals united, but, on analysis, appreciable quantities of the gold

were detected even at a distance of more than 5 millimetres from the common surface, while within a distance of three-quarters of a millimetre from the surface gold had penetrated into the lead to the extent of 1 oz. 6 dwts. per ton, an amount which could have been profitably extracted.

Whether it is or is not possible to devise any other intelligible account of the cause of such phenomena, it is certain that a simple and adequate explanation is found in the hypothesis that matter consists of discrete parts in a state of motion, which can penetrate into the spaces between the corresponding parts of surrounding bodies.

The hypothesis thus framed is also the only one which affords a rational explanation of other simple and well-known facts. If matter is regarded as a continuous medium the phenomena of expansion are unintelligible. There is, apparently, no limit to the expansion of matter, or, to fix our attention on one kind of matter, let us say to the expansion of a gas; but it is inconceivable that a continuous material which fills or is present in every part of a given space could also be present in every part of a space a million times as great. Such a statement might be made of a mathematical abstraction; it cannot be true of any real substance or thing. If, however, matter consists of discrete particles, separated from each other either by empty space or by something different from themselves, we can at once understand that expansion and contraction may be nothing more than the mutual separation or approach of these particles.

Again, no clear mental picture can be formed of the phenomena of heat unless we suppose that heat is a mode of motion. In the words of Rumford, it is "extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in [his] experiment [on friction] except it be motion (*Phil. Trans.*, 1798, p. 99). And if heat be motion there can be no doubt that it is the fundamental particles of matter which are moving. For the motion is not visible, is not motion of the body as a whole, while diffusion, which is a movement of matter, goes on more quickly as the temperature rises, thereby proving that the internal motions have become more rapid, which is exactly the result which would follow if these were the movements which constitute sensible heat.

Combining, then, the phenomena of diffusion, expansion, and heat, it is not too much to say that no hypotheses which make them intelligible have ever been framed other than those which are at the basis of the atomic theory.

Many other considerations also point to the same conclusion. Many years ago Lord Kelvin gave independent arguments, based on the properties of gases, on the constitution of the surfaces of liquids, and on the electric properties of metals, all of which indicate that matter is, to use his own phrase, coarse-grained—that it is not identical in constitution throughout, but that adjacent minute parts are distinguishable from each other by being either of different natures or in different states.

And here it is necessary to insist that all these fundamental proofs are independent of the nature of the particles or granules into which matter must be divided.

The particles, for instance, need not be different in kind from the medium which surrounds and separates them. It would suffice if they were what may be called singular parts of the medium itself, differing from the rest only in some peculiar state of internal motion or of distortion, or by being in some other way earmarked as distinct individuals. The view that the constitution of matter is atomic may and does receive support from theories in which definite assumptions are made as to the constitution of the atoms; but when, as is often the case, these assumptions introduce new and more recondite difficulties, it must be remembered that the fundamental hypothesis—that matter consists of discrete parts, capable of independent motions—is forced upon us by facts and arguments

which are altogether independent of what the nature and properties of these separate parts may be.

As a matter of history the two theories, which are not by any means mutually exclusive, that atoms are particles which can be treated as distinct in kind from the medium which surrounds them, and that they are parts of that medium existing in a special state, have both played a large part in the theoretical development of the atomic hypothesis. The atoms of Waterston, Clausius, and Maxwell were particles. The vortex-atoms of Lord Kelvin, and the strain atoms (if I may call them so) suggested by Mr. Larmor, are states of a primary medium which constitutes a physical connection between them, and through which their mutual actions arise and are transmitted.

Properties of the Basis of Matter.

It is easy to show that, whichever alternative be adopted, we are dealing with something, whether we consider it under the guise of separate particles or of differentiated portions of the medium, which has properties different from those of matter in bulk.

For if the basis of matter had the same constitution as matter, the irregular heat movements could hardly be maintained either against the viscosity of the medium or the frittering away of energy of motion which would occur during the collisions between the particles. Thus, even in the case in which a hot body is prevented from losing heat to surrounding objects, its sensible heat should spontaneously decay by a process of self-cooling. No such phenomenon is known, and though on this, as on all other points, the limits of our knowledge are fixed by the uncertainty of experiment, we are compelled to admit that, to all appearance, the fundamental medium, if it exists, is unlike a material medium, in that it is non-viscous; and that the particles, if they exist, are so constituted that energy is not frittered away when they collide. In either case, we are dealing with something different from matter itself in the sense that, though it is the basis of matter, it is not identical in all its properties with matter.

The idea therefore that entities exist possessing properties different from those of matter in bulk is not introduced at the end of a long and recondite investigation to explain facts with which none but experts are acquainted. It is forced upon us at the very threshold of our study of Nature. Either the properties of matter in bulk cannot be referred to any simpler structure, or that simpler structure must have properties different from those of matter in bulk as we directly knew it—properties which can only be inferred from the results which they produce.

No *a priori* argument against the possibility of our discovering the existence of quasi-material substances, which are nevertheless different from matter, can prove the negative proposition that such substances cannot exist. It is not a self-evident truth that no substance other than ordinary matter can have an existence as real as that of matter itself. It is not axiomatic that matter cannot be composed of parts whose properties are different from those of the whole. To assert that even if such substances and such parts exist no evidence however cogent could convince us of their existence, is to beg the whole question at issue; to decide the cause before it has been heard.

We must therefore adhere to the standpoint adopted by most scientific men, viz., that the question of the existence of ultra-physical entities, such as atoms and the ether, is to be settled by the evidence, and must not be ruled out as inadmissible on *a priori* grounds.

On the other hand, it is impossible to deny that, if the mere entry on the search for the concealed causes of physical phenomena is not a trespass on ground we have no right to explore, it is at all events the beginning of a dangerous journey.

The wraiths of phlogiston, caloric, luminiferous corpuscles, and a crowd of other phantoms haunt the investigator, and as the grim host vanishes into nothingness he

cannot but wonder if his own conceptions of atoms and of the ether

"shall dissolve,
And, like this insubstantial pageant faded,
Leave not a wrack behind."

But though science, like Bunyan's hero, has sometimes had to pass through the "Valley of Humiliation," the spectres which meet it there are not really dangerous if they are boldly faced. The facts that mistakes have been made, that theories have been propounded, and for a time accepted, which later investigations have disproved, do not necessarily discredit the method adopted. In scientific theories, as in the world around us, there is a survival of the fittest, and Dr. James Ward's unsympathetic account of the blunders of those whose work, after all, has shed glory on the Nineteenth Century, might *mutatis mutandis* stand for a description of the history of the advance of civilisation. "The story of the progress so far," he tells us, "is briefly this: Divergence between theory and fact one part of the way, the wreckage of abandoned fictions for the rest, with an unattainable goal of phenomenal nihilism and ultra-physical mechanism beyond" (James Ward, "Naturalism and Agnosticism," vol. i., p. 153).

"The path of progress," says Professor Karl Pearson, "is strewn with the wreck of nations. Traces are everywhere to be seen of the hecatombs of inferior races, and of victims who found not the narrow way to the greater perfection. Yet these dead peoples are, in very truth, the stepping-stones on which mankind has arisen to the higher intellectual and deeper emotional life of to-day" (Karl Pearson, "National Life from the Standpoint of Science," p. 62).

It is only necessary to add that the progress of society is directed towards an unattainable goal of universal contentment, to make the parallel complete.

And so, in the one case as in the other, we may leave "the dead to bury their dead." The question before us is not whether we too may not be trusting to false ideas, erroneous experiments, evanescent theories. No doubt we are; but, without making an insolent claim to be better than our fathers, we may fairly contend that, amid much that is uncertain and temporary, some of the fundamental conceptions, some of the root-ideas of science, are so grounded on reason and fact that we cannot but regard them as an aspect of the very truth.

Enough has, perhaps, now been said on this point for my immediate purpose. The argument as to the constitution of matter could be developed further in the manner I have hitherto adopted, viz., by series of propositions, the proof of each of which is based upon a few crucial phenomena. In particular, if matter is divided into moving granules or particles, the phenomenon of cohesion proves that there must be mutual actions between them analogous to those which take place between large masses of matter, and which we ascribe to force, thereby indicating the regular, unvarying operation of active machinery which we have not yet the means of adequately understanding. For the moment, I do not wish to extend the line of reasoning that has been followed. My main object is to show that the notion of the existence of ultra-physical entities and the leading outlines of the atomic theory are forced upon us at the beginning of our study of Nature, not only by *a priori* considerations, but in the attempt to comprehend the results of even the simplest observation. These outlines cannot be effaced by the difficulties which undoubtedly arise in filling up the picture. The cogency of the proof that matter is coarse-grained is in no way affected by the fact that we may have grave doubts as to the nature of the granules. Nay, it is of the first importance to recognise that, though the fundamental assumptions of the atomic theory receive overwhelming support from a number of more detailed arguments, they are themselves almost of the nature of axioms, in that the simplest phenomena are unintelligible if they are abandoned.

The Range of the Atomic Theory.

It would be most unfair, however, to the atomic theory to represent it as depending on one line of reasoning only, or to treat its evidence as bounded by the very general propositions I have discussed.

It is true that as the range of the theory is extended the fundamental conception that matter is granular must be expanded and filled in by supplementary hypotheses as to the constitution of the granules. It may also be admitted that no complete or wholly satisfactory description of that constitution can as yet be given; that perfection has not yet been attained here or in any other branch of science; but the number of facts which can be accounted for by the theory is very large compared with the number of additional hypotheses which are introduced; and the cumulative weight of the additional evidence obtained by the study of details is such as to add greatly to the strength of the conviction that, in its leading outlines, the theory is true.

It was originally suggested by the facts of chemistry, and though, as we have seen, a school of chemists now thrusts it into the background, it is none the less true, in the words of Dr. Thorpe, that "every great advance in chemical knowledge during the last ninety years finds its interpretation in [Dalton's] theory" (Thorpe "Essays on Historical Chemistry," 1894, p. 368).

The principal mechanical and thermal properties of gases have been explained, and in large part discovered, by the aid of the atomic theory; and, though there are outstanding difficulties, they are, for the most part, related to the nature of the atoms and molecules, and do not affect the question as to whether they exist.

The fact that different kinds of light all travel at the same speed in interplanetary space, while they move at different rates in matter, is explained if matter is coarse-grained. But to attempt to sum up all this evidence would be to recite a text-book on physics. It must suffice to say that it is enormous in extent and varied in character, and that the atomic theory imparts a unity to all the physical sciences which has been attained in no other way.

I must, however, give a couple of instances of the wonderful success which has been achieved in the explanation of physical phenomena by the theory we are considering, and I select them because they are in harmony with the line of argument I have been pursuing.

When a piece of iron is magnetised its behaviour is different according as the magnetic force applied to it is weak, moderate, or strong. When a certain limit is passed the iron behaves as a non-magnetic substance to all further additions of magnetic force. With strong forces it does and with very weak forces it does not remain magnetised when the force ceases to act. Professor Ewing has imitated all the minute details of these complicated properties by an arrangement of small isolated compass needles to represent the molecules. It may fairly be said that as far as this particular set of phenomena is concerned a most instructive working model based on the molecular theory has not only been imagined but constructed.

The next illustration is no less striking. We may liken a crowd of molecules to a fog; but while the fog is admitted by everybody to be made up of separate globules of water, the critics of scientific method are sometimes apt to regard the molecules as mere fictions of the imagination. If, however, we could throw the molecules of a highly rarefied gas into such a state that vapour condensed on them, so that each became the centre of a water-drop, till the host of invisible molecules was, as it were, magnified by accretion into a visible mist, surely no stronger proof of their reality could be desired. Yet there is every reason to believe that something very like this has been accomplished by Mr. C. T. R. Wilson and Professor J. J. Thomson.

It is known that it is comparatively difficult to produce a fog in damp air if the mixture consists of air and water-

vapour alone. The presence of particles of very fine dust facilitates the process. It is evident that the vapour condenses on the dust particles and that a nucleus of some kind is necessary on which each drop may form. But electrified particles also act as nuclei; for if a highly-charged body from which electricity is escaping be placed near a steam-jet, the steam condenses; and a cloud is also formed in dust-free air more easily than would otherwise be the case if electricity is discharged into it.

Again, according to accepted theory, when a current of electricity flows through a gas some of the atoms are divided into parts which carry positive and negative charges as they move in opposite directions, and unless this breaking-up occurs a gas does not conduct electricity. But a gas can be made a conductor merely by allowing the Röntgen rays or the radiation given off by uranium to fall upon it. A careful study of the facts shows that it is probable that some of the atoms have been broken up by the radiation, and that their oppositely electrified parts are scattered among their unaltered fellows. Such a gas is said to be ionised.

Thus by these two distinct lines of argument we come to the conclusions:—1st, That the presence of electrified particles promotes the formation of mist; and, 2nd, that in an ionised gas such electrified particles are provided by the breaking-up of atoms.

The two conclusions will mutually support each other if it can be shown that a mist is easily formed in ionised air. This was tested by Mr. Wilson, who showed that in such air mist is formed as though nuclei were present, and thus in the cloud we have visible evidence of the presence of the divided atoms. If then we cannot handle the individual molecules we have at least some reason to believe that a method is known of seizing individuals, or parts of individuals, which are in a special state, and of wrapping other matter round them till each one is the centre of a discrete particle of a visible fog.

I have purposely chosen this illustration, because the explanation is based on a theory—that of ionisation—which is at present subjected to hostile criticism. It assumes that an electrical current is nothing more than the movement of charges of electricity. But magnets placed near an electric current tend to set themselves at right-angles to its direction; a fact on which the construction of telegraphic instruments is based. Hence if the theory be true, a similar effect ought to be produced by a moving charge of electricity. This experiment was tried many years ago in the laboratory of Helmholtz by Rowland, who caused a charged disc to spin rapidly near a magnet. The result was in accord with the theory; the magnet moved as though acted upon by an electric current. Of late, however, M. Crémieu has investigated the matter afresh, and has obtained results which, according to his interpretation, were inconsistent with that of Rowland.

M. Crémieu's results are already the subject of controversy (see *Phil. Mag.*, July, 1901, p. 144; and *Johns Hopkins University Circulars*, xx., No. 152, May—June, 1901, p. 78), and are, I believe, likely to be discussed in the Section of Physics. This is not the occasion to enter upon a critical discussion of the question at issue, and I refer to it only to point out that though, if M. Crémieu's result were upheld, our views as to electricity would have to be modified, the foundations of the atomic theory would not be shaken.

It is, however, from the theory of ions that the most far-reaching speculations of science have recently received unexpected support. The dream that matter of all kinds will some day be proved to be fundamentally the same has survived many shocks. The opinion is consistent with the great generalisation that the properties of elements are a periodic function of their atomic weights. Sir Norman Lockyer has long been a prominent exponent of the view that the spectra of the stars indicate the reduction of our so-called elements to simpler forms, and now Professor J. J. Thomson believes that we can break off from an atom a part, the mass of which is not more than one-thousandth

of the whole, and that these corpuscles, as he has named them, are the carriers of the negative charge in an electric current. If atoms are thus complex, not only is the *a priori* probability increased that the different structures which we call elements may all be built of similar bricks, but the discovery by Lenard that the ease with which the corpuscles penetrate different bodies depends only on the density of the obstacles, and not on their chemical constitution, is held by Professor Thomson to be "a strong confirmation of the view that the atoms of the elementary substances are made up of simpler parts, all of which are alike."* On the present occasion, however, we are occupied rather with the foundations than with these ultimate ramifications of the atomic theory; and having shown how wide its range is, I must, to a certain extent, retrace my steps and return to the main line of my argument.

The Properties of Atoms and Molecules.

For if it be granted that the evidence that matter is coarse grained and is formed of separate atoms and molecules is too strong to be resisted, it may still be contended that we can know little or nothing of the sizes and properties of the molecules.

It must be admitted that though the fundamental postulates are always the same, different aspects of the theory, which have not in all cases been successfully combined, have to be developed when it is applied to different problems; but in spite of this there is little doubt that we have some fairly accurate knowledge of molecular motions and magnitudes.

If a liquid is stretched into a very thin film, such as a soap bubble, we should expect indications of a change in its properties when the thickness of the film is not a very large multiple of the average distance between two neighbouring molecules. In 1890 Sohncke (*Wied. Ann.*, 1890, xl., pp. 345–355), detected evidence of such a change in films of the average thickness of 106 millionths of a millimetre (μ), and quite recently Rudolph Weber found it in an oil-film when the thickness was 115 μ (*Ann. der Phys.*, 1901, iv., pp. 706–721).

Taking the mean of these numbers and combining the results of different variants of the theory we may conclude that a film should become unstable, and tend to rupture spontaneously somewhere between the thicknesses of 110 and 55 μ , and Professor Reinold and I found by experiment that this instability is actually exhibited between the thicknesses of 96 and 45 μ (*Phil. Trans.*, 1893, 184, pp. 505–529). There can therefore be little doubt that the first approach to molecular magnitudes is signalled when the thickness of a film is somewhat less than 100 μ , or 4 millionths of an inch.

Thirteen years ago I had the honour of laying before the Chemical Society a *résumé* of what was then known on these subjects (*Chem. Soc. Trans.*, March, 1888, liii., pp. 222–262), and I must refer to that lecture or to the most recent edition of O. E. Meyer's work on the kinetic theory of gases ("Kinetic Theory of Gases," O. E. Meyer, 1899, translated by R. E. Baynes), for the evidence that various independent lines of argument enable us to estimate quantities very much less than 4 millionths of an inch, which is perhaps from 500 to 1000 times greater than the magnitude which, in the present state of our knowledge, we can best describe as the diameter of a molecule.

Confining our attention, however, to the larger quantities, I will give one example to show how strong is the cumulative force of the evidence as to our knowledge of the magnitudes of molecular quantities.

We have every reason to believe that though the molecules in a gas frequently collide with each other, yet in the case of the more perfect gases the time occupied in collisions is small compared with that in which each molecule travels undisturbed by its fellows. The average

distance travelled between two successive encounters is called the mean free path, and, for the reason just given, the question of the magnitude of this distance can be attacked without any precise knowledge of what a molecule is, or of what happens during an encounter.

Thus the mean free path can be determined, by the aid of the theory, either from the viscosity of the gas or from the thermal conductivity. Using figures given in the latest work on the subject (Meyer's "Kinetic Theory of Gases," see above), and dealing with one gas only, as a fair sample of the rest, the lengths of the mean free path of hydrogen as determined by these two independent methods differ only by about 3 per cent. Further, the mean of the values which I gave in the lecture already referred to differed only by about 6 per cent from the best modern result, so that no great change has been introduced during the last thirteen years.

It may, however, be argued that these concordant values are all obtained by means of the same theory, and that a common error may affect them all. In particular, some critics have of late been inclined to discredit the atomic theory by pointing out that the strong statements which have sometimes been made as to the equality, among themselves, of atoms or molecules of the same kind may not be justified, as the equality may be that of averages only, and be consistent with a considerable variation in the sizes of individuals.

Allowing this argument more weight than it perhaps deserves, it is easy to show that it cannot affect seriously our knowledge of the length of the mean free path.

Professor George Darwin (*Phil. Trans.*, 180), has handled the problem of a mixture of unequal spherical bodies in the particular case in which the sizes are distributed according to the law of errors, which would involve far greater inequalities than can occur among atoms. Without discussing the precise details of his problem it is sufficient to say that in the case considered by him the length of the mean free path is $\frac{1}{\sqrt{2}}$ of what it would be if the particles were equal. Hence were the inequalities of atoms as great as in this extreme case, the reduction of the mean free path in hydrogen could only be from 185 to 119 μ ; but they must be far less, and therefore the error, if any, due to this cause could not approach this amount. It is probably inappreciable.

Such examples might be multiplied, but the one I have selected is perhaps sufficient to illustrate my point, viz., that considerable and fairly accurate knowledge can be obtained as to molecular quantities by the aid of theories the details of which are provisional, and are admittedly capable of improvement.

Is the Model Unique?

But the argument that a correct result may sometimes be obtained by reasoning on imperfect hypotheses raises the question as to whether another danger may not be imminent. To be satisfactory our model of Nature must be unique, and it must be impossible to imagine any other which agrees equally well with the facts of experiment. If a large number of hypotheses could be framed with equal claims to validity, that fact would alone raise grave doubts as to whether it were possible to distinguish between the true and the false. Thus Professor Poincaré has shown that an infinite number of dynamical explanations can be found for any phenomenon which satisfies certain conditions. But though this consideration warns us against the too ready acceptance of explanations of isolated phenomena, it has no weight against a theory which embraces so vast a number of facts as those included by the atomic theory. It does not follow that, because a number of solutions are all formally dynamical, they are therefore all equally admissible. The pressure of a gas may be explained as the result of a shower of blows delivered by molecules, or by a repulsion between the various parts of a continuous medium. Both solutions are expressed in dynamical language; but one is, and the other is not, compatible with the observed phenomena of

* For the most recent account of this subject see an article on "Bodies smaller than Atoms," by Professor J. J. Thomson in the *Popular Science Monthly* (The Science Press), August, 1901.

expansion. The atomic theory must hold the field until another can be found which is not inferior as an explanation of the fundamental difficulties as to the constitution of matter, and is, at the same time, not less comprehensive.

On the whole, then, the question as to whether we are attempting to solve a problem which has an infinite number of solutions may be put aside until one solution has been found which is satisfactory in all its details. We are in a sufficient difficulty about that to make the rivalry of a second of the same type very improbable.

The Phenomena of Life.

But it may be asked—nay, it has been asked—may not the type of our theories be radically changed? If this question does not merely imply a certain distrust in our own powers of reasoning, it should be supported by some indication of the kind of change which is conceivable.

Perhaps the chief objection which can be brought against physical theories is that they deal only with the inanimate side of Nature, and largely ignore the phenomena of life. It is therefore in this direction, if in any, that a change of type may be expected. I do not propose to enter at length upon so difficult a question, but, however we may explain or explain away the characteristics of life, the argument for the truth of the atomic theory would only be affected if it could be shown that living matter does not possess the thermal and mechanical properties, to explain which the atomic theory has been framed. This is so notoriously not the case that there is the gravest doubt whether life can in any way interfere with the action within the organism of the laws of matter in bulk belonging to the domain of mechanics, physics, and chemistry.

Probably the most cautious opinion that could now be expressed on this question is that, in spite of some outstanding difficulties which have recently given rise to what is called Neovitalism, there is no conclusive evidence that living matter can suspend or modify any of the natural laws which would affect it if it were to cease to live. It is possible that though subject to these laws the organism while living may be able to employ, or even to direct, their action within itself for its own benefit, just as it unquestionably does make use of the processes of external nature for its own purposes; but if this be so, the seat of the controlling influence is so withdrawn from view that on the one hand its very existence may be denied, while, on the other hand, Professor Hæckel, following Vogt, has recently asserted that "matter and ether are not dead, and only moved by extrinsic force; but they are endowed with sensation and will; they experience an inclination for condensation, a dislike for strain; they strive after the one, and struggle against the other" (*"Riddle of the Universe,"* English translation, 1900, p. 380).

But neither unproved assertions of this kind nor the more refined attempts that have been made by others to bring the phenomena of life and of dead matter under a common formula touch the evidence for the atomic theory. The question as to whether matter consists of elements capable of independent motion is prior to, and independent of, the further questions as to what these elements are, and whether they are alive or dead.

The physicist, if he keeps to his business asserts, as the bases of the atomic theory, nothing more than that he who declines to admit that matter consists of separate moving parts must regard many of the simplest phenomena as irreconcilable and unintelligible, in spite of the fact that means of reconciling them are known to everybody, in spite of the fact that the reconciling theory gives a general correlation of an enormous number of phenomena in every branch of science, and that the outstanding difficulties are connected, not so much with the fundamental hypotheses that matter is composed of distinguishable entities which are capable of separate motions as with the much more difficult problem of what these entities are.

On these grounds the physicist may believe that, though he cannot handle or see them, the atoms and molecules are as real as the ice crystals in a cirrus cloud which he cannot reach; as real as the unseen members of a meteoric swarm whose death-glow is lost in the sunshine, or which sweep past us, unentangled, in the night.

If the confidence that his methods are weapons with which he can fight his way to the truth were taken from the scientific explorer, the paralysis which overcomes those who believe that they are engaged in a hopeless task would fall upon him.

Physiology has specially flourished since physiologists have believed that it is possible to master the physics and chemistry of the framework of living things, and since they have abandoned the attitude of those who placed in the foreground the doctrine of the vital force. To supporters of that doctrine the principle of life was not a hidden directing power which could perhaps whisper an order that the flood-gates of reservoirs of energy should now be opened and now closed, and could, at the most, work only under immutable conditions to which the living and the dead must alike submit. On the contrary, their vital force pervaded the organism in all its parts. It was an active and energetic opponent of the laws of physics and chemistry. It maintained its own existence not by obeying but by defying them; and though destined to be finally overcome in the separate campaigns of which each individual living creature is the scene, yet like some guerilla chieftain it was defeated here only to reappear there with unabated confidence and apparently undiminished force.

This attitude of mind checked the advance of knowledge. Difficulty could be evaded by a verbal formula of explanation which in fact explained nothing. If the mechanical, or physical, or chemical causes of a phenomenon did not lie obviously upon the surface, the investigator was tempted to forego the toil of searching for them below; it was easier to say that the vital force was the cause of the discrepancy, and that it was hopeless to attempt to account for the action of a principle which was incomprehensible in its nature.

For the physicist the danger is no less serious though it lies in a somewhat different direction. At present he is checked in his theories by the necessity of making them agree with a comparatively small number of fundamental hypotheses. If this check were removed his fancy might run riot in the wildest speculations, which would be held to be legitimate if only they led to formulæ in harmony with facts. But the very habit of regarding the end as everything, and the means by which it was attained as unimportant, would prevent the discovery of those fragments of truth which can only be uncovered by the painful process of trying to make inconsistent theories agree, and using all facts, however remote, as the tests of our central generalisation.

"Science," said Helmholtz, "Science, whose every object it is to comprehend Nature, must start with the assumption that Nature is comprehensible." And again:—"The first principle of the investigator of Nature is to assume that Nature is intelligible to us, since otherwise it would be foolish to attempt the investigation at all." These axioms do not assume that all the secrets of the universe will ultimately be laid bare, but that a search for them is hopeless if we undertake the quest with the conviction that it will be in vain. As applied to life they do not deny that in living matter something may be hidden which neither physics nor chemistry can explain, but they assert that the action of physical and chemical forces in living bodies can never be understood, if at every difficulty and at every check in our investigations we desist from further attempts in the belief that the laws of physics and chemistry have been interfered with by an incomprehensible vital force. As applied to physics and chemistry they do not mean that all the phenomena of life and death will ultimately be included in some simple and self-sufficing mechanical theory; they do mean that we are not to sit down contented with paradoxes such as that the same thing can fill

both a large space and a little one; that matter can act where it is not, and the like, if by some reasonable hypothesis, capable of being tested by experiment, we can avoid the acceptance of these absurdities. Something will have been gained if the more obvious difficulties are removed, even if we have to admit that in the background there is much that we cannot grasp.

The Limits of Physical Theories.

And this brings me to my last point. It is a mistake to treat physical theories in general, and the atomic theory in particular, as though they were parts of a scheme which has failed if it leaves anything unexplained, which must be carried on indefinitely on exactly the same principles, whether the ultimate results are, or are not, repugnant to common sense.

Physical theories begin at the surface with phenomena which directly affect our senses. When they are used in the attempt to penetrate deeper into the secrets of Nature it is more than probable that they will meet with insuperable barriers, but this fact does not demonstrate that the fundamental assumptions are false, and the question as to whether any particular obstacle will be for ever insuperable can rarely be answered with certainty.

Those who belittle the ideas which have of late governed the advance of scientific theory too often assume that there is no alternative between the opposing assertions that atoms and the ether are mere figments of the scientific imagination, or that, on the other hand, a mechanical theory of the atoms and of the ether, which is now confessedly imperfect, would, if it could be perfected, give us a full and adequate representation of the underlying realities.

For my own part I believe that there is a *via media*.

A man peering into a darkened room, and describing what he thinks he sees, may be right as to the general outline of the objects he discerns, wrong as to their nature and their precise forms. In his description fact and fancy may be blended, and it may be difficult to say where the one ends and the other begins; but even the fancies will not be worthless if they are based on a fragment of truth, which will prevent the explorer from walking into a looking-glass, or stumbling over the furniture. He who saw "men as trees walking" had at least a perception of the fundamental fact that something was in motion around him.

And so, at the beginning of the twentieth century, we are neither forced to abandon the claim to have penetrated below the surface of Nature, nor have we, with all our searching, torn the veil of mystery from the world around us.

The range of our speculations is limited both in space and time; in space, for we have no right to claim, as is sometimes done, a knowledge of the "infinite universe"; in time, for the cumulative effects of actions which might pass undetected in the short span of years of which we have knowledge, may, if continued long enough, modify our most profound generalisations. If some such theory as the vortex-atom theory were true, the faintest trace of viscosity in the primordial medium would ultimately destroy matter of every kind. It is thus a duty to state what we believe we know in the most cautious terms, but it is equally a duty not to yield to mere vague doubts as to whether we can know anything.

If no other conception of matter is possible than that it consists of distinct physical units—and no other conception has been formulated which does not blur what are otherwise clear and definite outlines—if it is certain, as it is, that vibrations travel through space which cannot be propagated by matter, the two foundations of physical theory are well and truly laid. It may be granted that we have not yet framed a consistent image either of the nature of the atoms or of the ether in which they exist; but I have tried to show that in spite of the tentative nature of some of our theories, in spite of many outstanding difficulties, the atomic theory unifies so many

facts, simplifies so much that is complicated, that we have a right to insist—at all events till an equally intelligible rival hypothesis is produced—that the main structure of our theory is true; that atoms are not merely helps to puzzled mathematicians, but physical realities.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 101).

D. Solubility of the Nitrocelluloses in Ether-alcohol.

The soluble nitration stages of cellulose play an important part in different industries, and octo- and enne-nitrocellulose are more especially to be considered in this respect. But, as we have seen, these two nitration products do not indicate the limits of solubility; soluble products were obtained nearly down to heptanitrocellulose, and as far up as decanitrocellulose. These limiting cases are naturally less easily obtained than the middle products, as there is always the danger of forming traces of the lower or higher insoluble stages. Hence, if the nitrogen content does not come into consideration, and it is of sole importance to produce a completely soluble body, products with 174—184 c.c. NO are best adapted to the purpose. These nitrocelluloses are said to be insoluble in alcohol; those obtained by us were insoluble in 95 per cent alcohol, but were soluble in absolute alcohol, and, on the other hand, were insoluble in absolute ether. Hence, we might be inclined to think that, in the mixtures of ether and alcohol, the latter is the real solvent. But it appeared that the solubility in absolute alcohol did not run parallel with that in ether-alcohol; from enne-nitrocellulose upwards the former diminishes rapidly.

The already mentioned solubility determinations refer to an ether-alcohol mixture of 3 : 1. A few more experiments were now started to determine to what extent this ratio may be varied without diminishing the solubility. (The product in question yielded 184 c.c. NO). With an ether-alcohol mixture of 6 : 1 complete solution was easily effected; with one of 9 : 1 the solubility began to become difficult, 95 per cent being still dissolved; in a mixture of 12 ether and 1 alcohol 92·1 per cent dissolved. With further diminution of the proportion of alcohol the solubility rapidly diminished; with the ratio 27 : 1 7·3 per cent was dissolved.

The converse was now investigated, viz., the extent to which the proportion of ether may be diminished. With an ether-alcohol mixture $\frac{3}{2}$: 1 complete solution easily resulted; with the ratio $\frac{1}{2}$: 1 solution became difficult, only 92 per cent dissolved after treating twice with the mixture; with the ratio $\frac{1}{12}$: 1 it was remarkable that solution became again more easy, 96 per cent being dissolved after only one treatment; even with the mixture $\frac{1}{24}$: 1 95·6 per cent was dissolved. Hence, it is obvious that the alcohol plays the most important part in the mixture.

E. Formula of Kisniemsky.

A research of Kisniemsky appeared recently, in which an attempt was made to express in a simple ratio the relation between the composition of the nitration mixtures and the properties of the corresponding nitration products. The composition of the nitration mixture is brought into the form $xN_2O_5 \cdot H_2O + aSO_3 \cdot H_2O + cH_2O$, and the magnitude, $(1+a)-c=\mu$, is called the characteristic of the mixture. The nitration mixtures with $\mu > 0$ should produce highly nitrated, slightly soluble products; those, on the other hand, with $\mu < 0$ should give soluble products, and those in which μ rises but little above the value -1 products with the highest possible proportion of nitrogen.

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

Our results were now reckoned in a similar manner, and, in general, they were in agreement with the above. But when μ nearly = 0 this value (as Kisniemsky himself has already observed) gives no result; between -0.3 and +0.3 there can be no reliable prediction of the properties. But this interval includes numerous important cases. In the others, also, the conclusion, especially as regards the proportion of nitrogen, is so indefinite that it forms no basis on which a nitration on the large scale could be conducted. Again, it is not to be inferred that the relation between the composition of the nitration mixture and the different properties of the corresponding nitrocelluloses can be expressed by so simple a formula.

F. Influence of the amount of Nitrous Acid contained in the Nitric Acid on the Percentage of Nitrogen and the Gain of Nitrocellulose.

The above mentioned nitrations were carried out with acid mixtures free from nitrous acid. As the amount of free nitrous acid in such mixtures is proportional to the degree of dilution, there is a considerable quantity of nitrous acid present with 10 per cent of water, while in concentrated acid mixtures this must all be converted into nitrosyl-sulphuric acid and nitric acid. Lunge and Weintraub have already proved that in this form it does not disturb the process of nitration; it still remained to investigate if this is also the case when the nitrous acid is retained as such in the nitration mixture.

The acid mixture used for this purpose had the following composition: -60.71 per cent H_2SO_4 , 30.67 per cent HNO_3 , 8.62 per cent H_2O . Hence the ratio of sulphuric acid to nitric acid was 1.98 : 1.

Equal portions of this mixture were treated with different quantities of nitrous acid. In this case also, up to a proportion of nitrous acid which would scarcely exist in practice, it is not possible to detect its influence either in regard to the percentage of nitrogen of the product or to the gain. This was of importance to us; for in the reverse case the results for obtaining higher nitration stages with dilute acid mixtures would have lost in practical significance.

TABLE XVII.

Expt.	C.c. NO per 1 grm.	N per cent.	Gain.	N_2O_5 per cent.
1.	216.15	13.55	174.53	0.13
2.	215.10	13.50	175.02	0.99
3.	216.30	13.56	173.98	0.84
4.	216.21	13.56	175.60	5.15

(To be continued).

THE ASSAYING OF COMPLEX GOLD ORES.*

By ERNEST A. SMITH, Assoc.R.S.M., F.C.S.,
late Assistant Instructor in Assaying, Royal School of Mines, London.

(Concluded from p. 100).

Auriferous Bismuth Ores.

ALTHOUGH not of frequent occurrence in nature, yet bismuth accompanies various ores of silver, and is also found occasionally associated with gold ores.

Bismuth is almost invariably found in nature in the metallic state; but occasionally it is met with as sulphide and as carbonate. It is also found in combination with tellurium associated with gold. Assays of auriferous bismuth ores are conducted like those of oxidised gold ores, but on account of the volatility of bismuth it is of importance that a readily fusible slag should be obtained, and for this purpose comparatively large quantities of sodium carbonate or of borax should be employed. When much bismuth is present the quantity of red-lead should be increased in order to effect its oxidation; a little nitre may also be added. Ores containing bismuth should not

be roasted. A piece of iron should be added in the case of ores containing bismuthine or pyritic material.

It is not essential to pass the whole of the bismuth into the slag, but it is advisable to do so, otherwise it alloys with the lead, and although bismuth works on the cupel as satisfactorily as lead, yet the amount of gold and silver absorbed by the cupel and volatilised is greater when bismuth is present (E. A. Smith, *Journ. Chem. Soc.*, 1894, vol. lxv., p. 624). The fusion of the ore is conducted at a comparatively low temperature. After pouring the charge the mould should be left undisturbed until the slag is quite cold, as the effect of bismuth when combined with lead is to form more readily fusible alloys which remain in a molten condition for a much longer period than lead. If the proportion of bismuth does not exceed that of the lead the alloys are malleable, but the malleability is diminished with an increase of bismuth. The lead buttons obtained from the fusion, if inconveniently large, may be reduced in weight by scorification, but the temperature employed for this purpose should be low on account of the volatility of bismuth.

Scorification Process.

Although complex ores poor in gold are as a general rule better assayed by the fusion process in order that a comparatively large quantity of material may be operated upon, the scorification process is especially applicable to complex ores rich in gold and to concentrates. It may be remarked that in Germany and the United States the scorification process is in many cases preferred to the crucible process for all classes of ore, as the operations are easy to conduct, and very little variation is needed in the treatment of the different classes of ore. If the ore is poor, several assays (sometimes eight or ten) are made, and the resulting lead buttons scorified together. The small quantity of ore that can be treated constitutes the chief disadvantage of the process.

When the gold is distributed through the ore in comparatively large particles, the presence of one or two particles of metallic gold in an assay may cause the result to be erroneous. The larger charges operated upon in the crucible process are likely to give results which are nearer than those of the smaller charges to the average richness of the parcel of ore from which they are taken.

The quantity of material operated upon and of lead required for the scorification process varies with the nature of the substance to be assayed. As a general rule, not more than from 5 to 10 grms. of material are used, as these are the largest quantities which can conveniently be treated unless scorifiers of unusual size are employed. The weight of granulated lead necessary is generally from ten to fifteen times the weight of the material taken, but sometimes as much as twenty times its weight or even more is required. In the case of ores containing substances which yield lead, the quantity of granulated lead may be reduced to five times the weight of material taken for assay according to circumstances. The employment of insufficient lead is usually indicated by the presence of imperfectly fused particles in the slag or on the scorifier, notwithstanding the fact that the temperature has been sufficiently high. In order to facilitate the formation of a fluid slag a little borax is placed on the top of the contents of the scorifier, but care should be taken not to use a large quantity at the commencement of the operation, otherwise the surface of the molten lead becomes covered, and its oxidation is retarded. A convenient quantity to employ for 5 grms. of material is 0.1 grm., but this may be increased in special cases. If the slag appears pasty when the temperature is sufficiently high, more borax may be added, but it would be more satisfactory to repeat the assay with a larger proportion of lead. A small quantity (0.1 to 0.25 grm.) of powdered glass or very fine siliceous sand may be added with advantage for ores rich in copper. The following table gives the proportions of lead and of borax found by experience to be best adapted to the

* Abstract of Paper read before Institution of Mining and Metallurgy, May 15, 1901.

different classes of ore. The proportions are referred to one part of the material to be assayed :—

Character of material.	For one part of material take—	
	Parts of granulated lead.	Parts of borax glass.
Antimonial	10 to 15	0'1 to 0'5
Arsenical		
Basic (FeO ₃ , Al ₂ O ₃ , CaO), &c.	10	0'25 to 1'0
Cupriferous	15 to 20	0'1 to 0'2
Fahlerz		
Galena and lead mineral ..	5 to 8	0'1
Pyritic (iron pyrites)	10 to 15	0'1 to 0'2
Siliceous	10	0'1
Zinc blende	10 to 15	0'1 to 0'2

The manipulation of the scorification process is too well known to need a detailed description here, but it may be pointed out that the losses frequently incurred are chiefly due to the employment of improper temperatures. The temperature, which is higher than that required for cupellation, should be well maintained during the process; if too low at first, gold and silver is liable to be retained in the slag. When the temperature has been too low, it is usually indicated by the occurrence of small white spots of lead sulphate on the surface of the slag after pouring. With very rich sulphides the results obtained are frequently much at variance with one another, which is probably due to the formation of oxysulphides (compounds of metallic oxides and sulphides), which remain in the slag, and retain considerable quantities of the precious metals. An excess of lead and a high temperature greatly help to prevent the formation of oxysulphides.

As a general rule, the loss of precious metals in the slag from scorification is small, but in the case of very rich ores it is always advisable to re-treat the slag. This may be done by re-scorifying in the same dish, or it may be fused in a crucible with suitable fluxes as previously described for slags from the crucible process.

Methods of "Concentration" for Poor Ores.

When assaying auriferous ores very poor in gold, the button of gold obtained from such quantities of ore (usually 50 grms.), as may be conveniently worked by the usual methods of assay is often so small as to require more than ordinary care in its manipulation.

In order to bring the button of gold within the scope of the balance and lessen the strain on the assayer's attention, larger charges of ore, of 100 or even 200 grms., are sometimes employed in the case of the poorest auriferous minerals. Large charges, however, are inconvenient, as they necessitate the use of large quantities of flux, and hence of very large crucibles. It is better, in the author's opinion, to make two independent fusions (or in exceptional cases three), each of 50 grms., and scorify the resulting lead buttons together, and repeat this process if necessary until the whole of the precious metals is concentrated in one button of lead of convenient size for cupellation. In the case of pyritic ores some assayers prefer to concentrate the precious metals in a regulus, which is subsequently treated for gold and silver.

Methods of concentration* for very poor ores have their advantages, but it must be admitted that they are usually tedious, laborious, and, to a considerable extent, uncertain. As the result of a series of experiments on the various methods of "concentration," the author has come to the conclusion that, although they may be advantageous in exceptional cases, as a general rule more satisfactory and trustworthy results are obtained by making independent fusions each of 50 grms. of ore, and concentrating the gold and silver in one button of lead as above indicated.

Summary.

The methods of assaying best adapted to the various complex ores enumerated may be summarised as follows:—

* Several methods of concentration are described in "Metallurgy of Gold," by T. K. Rose (see article on Assaying).

Basic Oxidised Ores.—Direct fusion, with special attention to the proportion of charcoal powder added to the charge, and the addition of metallic iron for ores containing a small percentage of pyritic material.

Pyritic Ores (mainly Iron Pyrites).—Roasting previous to fusion, and subsequent treatment as for basic ores. Fusion direct, with the addition of metallic iron, may be applied to ores containing 30 per cent or less of pyritic material. Oxidation with nitre can only be satisfactorily applied in cases where comparatively small quantities of pyritic material are present.

Arsenical Ores.—Preliminary roasting followed by fusion as for basic ores.

Antimonial Ores.—Generally oxidation with nitre.

Cupriferous Ores.—For ores rich in copper combined wet and dry methods. Ores comparatively poor in copper may be fused direct, or after a preliminary roasting, with the addition of suitable fluxes, due attention being given to the proportion of lead oxide added. The scorification process is convenient in cases where the ore is sufficiently rich in the precious metals to allow of this method being adopted.

Ores with Galena.—Fusion direct with addition of metallic iron. Roasting should not be attempted when much galena is present.

Ores with Blende.—Careful roasting and subsequent fusion as for basic ores, but with the addition of larger proportions of fluxes, which must be varied, according to the amount of zinc present.

Telluride Ores.—Fusion direct with very large proportions of lead oxide and ordinary fluxes. Scorification should on no account be employed.

Bismuth Ores.—Fusion direct as for basic ores. Scorification is not satisfactory when large quantities of bismuth are present.

Assay Office, Sheffield.

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A SUMMARY).

By HARRY C. JONES.

(Continued from p. 108).

Organic Solvents (continued).

Formic and Acetic Acids.—Quite an elaborate investigation on the dissociating power of formic acid was carried out by Zanninovich-Tessarini (*Zeit. Phys. Chem.*, xix., 251). He used chiefly the freezing-point method, but also determined the conductivity of a few salts in this solvent. He measured the freezing-point lowering of formic acid produced by the following substances, at dilutions ranging from 0'34 to 3'4 normal (and in some cases at even greater concentration):—Potassium, sodium, ammonium, and lithium chlorides; potassium, sodium, and ammonium bromides; hydrochloric, acetic, and trichloroacetic acids. A few of his results are given:—

Potassium chloride.		Sodium bromide.		Hydrochloric acid.	
Concent.	Diss.	Concent.	Diss.	Concent.	Diss.
Normal.	Per cent.	Normal.	Per cent.	Normal.	Per cent.
0'341	74	1'522	51	1'82	0
1'055	62	2'509	54	2'20	0
2'263	63	4'995	60		

Formic acid is, thus, one of the strongest dissociating solvents next to water. The behaviour of hydrochloric acid in this solvent is very surprising. It not only shows no dissociation in formic acid, but the molecules are actually polymerised. The conductivities of potassium and sodium chlorides in formic acid were found to be very

* *American Chemical Journal*, xxv., No. 3.

large, and hydrochloric acid showed considerable conductivity in this solvent, although the freezing-point lowering indicated polymerisation instead of dissociation. This may be due to the fact that while most of the molecules were polymerised into very large complexes, some few were dissociated into ions which carried the current.

Zanninovich-Tessarini (*Zeit. Phys. Chem.*, xix., 255), also determined the freezing-point lowering of acetic acid produced by sodium bromide and lithium chloride. The former gave normal values, indicating no dissociation, while the latter showed very marked polymerisation.

The conductivity of sulphuric acid in acetic acid has been measured by Jones (*Amer. Chem. Journ.*, xvi., 13), who found that the molecular conductivity, which was small at all dilutions, increased with the dilution to a certain point ($v=3$), and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the result obtained by Kablukoff (*Zeit. Phys. Chem.*, iv., 431), for hydrochloric acid in ether and in isoamyl alcohol.

The Nitriles.—The conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate and silver nitrate, in propionitrile, were determined by Dutoit and Aston (*Comptes Rendus*, cxxv., 240). This investigation was extended by Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 321), to solutions in acetonitrile and butyronitrile. The dissociating power of these three related substances can be seen from the following figures:—

Silver nitrate.	Acetonitrile.	Propionitrile.	Butyronitrile.
	$\mu v.$	$\mu v.$	$\mu v.$
$v = 8$	54.5	14.21	—
$v = 128$	118.3	34.42	23.8
$v = 256$	131.5	38.86	35.5

The dissociating power is obviously greater in the first members of the series of nitriles, and becomes less as we ascend the series.

(To be continued).

NOTES AND QUERIES.

*. * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Cerite.—Can any reader inform me how to estimate quantitatively the Ce, La, Di, Nb, and Ta in cerite, or tell me where I could find this information?—**CERITE.**

Iron-mould Spots.—Can any reader give me a recipe whereby iron-mould spots and similar stains in old water-colour drawings can be removed without doing injury to the paper?—**H.**

GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.

DEPARTMENT OF CHEMISTRY.

EVENING CLASSES, providing complete

Courses of Instruction in various branches of Pure and Applied CHEMISTRY, are held at this Institute under the direction of Mr. ARTHUR LAPWORTH, D.Sc.(Lond.), F.I.C., &c. The Courses of Lectures and Practical Laboratory teaching are suitable for Students desiring to qualify in Chemistry at the Examinations of the London University, the Pharmaceutical Society, the Board of Education, and other public bodies. The equipment of the Chemical Laboratories has been considerably augmented and exceptional facilities are offered to advanced Students who desire to engage in Chemical Research Work during the Day or Evening. The new SESSION commences on SEPTEMBER 23rd. For further particulars apply to the Secretary.

J. S. REDMAYNE, B.A., Secretary.

NEW FAT-TRACTOR. Modification JERWITZ.

Apply for Pamphlet, 111, TRITONVILLE ROAD, DUBLIN.

GEORGE HERIOT'S TRUST. HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. LAURIE, M.A., D.Sc.

DAY TECHNICAL COLLEGE.

Three Years' Courses of Instruction in MECHANICAL ENGINEERING, ELECTRICAL ENGINEERING, TECHNICAL CHEMISTRY.

SESSION opens OCTOBER 1st and closes JUNE 6th, 1902. The Classes for the Diploma in Mechanical and Electrical Engineering are recognised by the University of Edinburgh, and Students wishing to obtain a B.Sc. in Engineering, as well as the Diploma, can qualify for the Degree by taking five additional courses in the University and passing the University examinations.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with special courses in Gas and Paper manufacture, Brewing, &c., by experts, in the third year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc. in Chemistry.

Matriculation fee, 5s.; Composition fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s.

There are also Art Classes, a class in Practice of Commerce, and classes for Agricultural Students in Mensuration, Chemistry, Physiography, Drawing, Handicraft, Land Surveying, Agricultural Engineering, Book-keeping, Bacteriology.

An Extract from the Calendar of the College, giving particulars, may be had on application at the College, or from the undersigned.

BURSARIES are from time to time given by the Governors to Students attending the College, and a Travelling Scholarship of £100 has been occasionally awarded to a deserving Student.

DAVID LEWIS, Treasurer.

Heriot Trust Chambers, 20, York Place,
Edinburgh, September 6, 1901.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The DIPLOMA of the COLLEGE is granted in the following Departments—CIVIL, MECHANICAL, ELECTRICAL, CHEMICAL, and MINING ENGINEERING; NAVAL ARCHITECTURE, ARCHITECTURE, METALLURGY, MATHEMATICS and PHYSICS, and CHEMISTRY.

The COURSES of STUDY for the Diploma extend over three Sessions. The average fee per Session is £12 12s. SPECIAL COURSES for individual Students are arranged as required. HOLDERS of the DIPLOMA are eligible for the DEGREE of B.Sc. in ENGINEERING of the UNIVERSITY of GLASGOW after attendance for one Session upon prescribed University Classes.

The LABORATORIES in the DEPARTMENTS of PHYSICS, CHEMISTRY, METALLURGY, MECHANICAL and ELECTRICAL ENGINEERING, are equipped with the most approved apparatus.

The SESSION opens SEPTEMBER 24th. ENTRANCE EXAMINATION begins SEPTEMBER 16th.

The CALENDAR (price by post 1s. 4d.) and PROSPECTUS (gratis) will be sent on application to the SECRETARY, 33, Bath Street, Glasgow.

ROYAL TECHNICAL INSTITUTE, SALFORD.

Principal—W. WILSON, M.A.

The next SESSION will open on SEPTEMBER 16th, 1901.

FULL DAY COURSES and EVENING CLASSES in various subjects, including CHEMISTRY, and DYEING and CALICO-PRINTING.

Special Course for Buyers and Salesmen in Textiles; also Course on Prints, &c., Analysis of Dyes, Dyewares, &c., and Gas Analysis.

Dyehouse contains Jigs and Plant for Experimental Dyeing of full width Calico, and in the Calico-printing Laboratory there is a complete range of full-sized Machinery.

Prospectus and particulars free on application.

RICHARD MARTIN, Secretary.

FOR SALE.

THE CHEMICAL GAZETTE.

Complete set (unbound), 17 Volumes, 1842—1859.
Price £4 4s. net.

Address "Gazette," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2182.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

GLASGOW, 1901.

By PERCY F. FRANKLAND, Ph.D., M.Sc., F.R.S., Professor
of Chemistry in the University of Birmingham.
President of the Section.

THE POSITION OF BRITISH CHEMISTRY AT THE DAWN OF THE TWENTIETH CENTURY.

Two circumstances unite in rendering this year especially appropriate for the survey and valuation of all departments of British life and organisation—the dawn of a new century, the close of the Victorian era. It is a moment when not only the nation as a whole, but every group of persons drawn together by whatever bond, and indeed each individual for himself, must involuntarily ask the question—Are we progressing or receding, or are we standing still? Upon us, then, who are bound together by the common interest which we have in that science to which this Section is devoted, there forces itself the question—What is the position of British Chemistry at the present moment, how does this present bear comparison with the past, and what are the prospects for the future?

To bring before you some considerations with respect to the answer which should be given to this question, or rather series of questions, will be my endeavour in responding to the honour which has been conferred on me of inaugurating the work of our Section at this Meeting of the Association.

It is with no light heart that I undertake this task, for there are present here to-day those whose much longer experience and far more intimate connection with the progress of our science render it presumption on my part to address them on this subject at all.

It is well known that the history of British Chemistry, as indeed that of British Science in general, is a very remarkable one; it is almost entirely made up of achievements which are the result of private initiative; and the persons who have taken part in the making of this history have, with some notable exceptions, not been servants of the State, and have thus differed from the makers of scientific history in almost every other country in the world. Thus the opportunities for the investigations which are recorded in the *Transactions* of our Chemical Society have, for the most part, not been provided out of the public purse, but by private individuals or by institutions which have been created by private benefaction.

This unique condition of things is well illustrated by taking up a volume of the Chemical Society's *Journal* and glancing at the table of contents.

Thus in the volume for 1881, taken at random, we find that, out of the seventy-five original communications which it contains, only thirteen emanate from Government laboratories, whilst what will surely not a little surprise the scientific historian of some centuries hence, is the circumstance that there are only four communications from the so-called "ancient seats of learning" of the United Kingdom, no fewer than three of which are by one and the same investigator. Again, most noteworthy is the fact that as many as five contributions are from distinguished amateurs. We have been told, on what many persons regard as high authority, that England is suffering from amateurism in all departments of life; and however true this may be as a general proposition, the amateurs of

British Science, like Gladstone, Schunck, and Perkin amongst living chemists, are assuredly some of the most valued possessions of this country.

On looking back a quarter of a century into the past, it is at once apparent how greatly during that short period of time—less than a generation of men—have the opportunities for higher chemical training been extended and multiplied in our midst. I think I shall not be far wrong in saying that until twenty-five years ago practically the only public laboratories in which the higher study of chemistry could be pursued were those of the Royal College of Chemistry, the Royal Institution, of University and King's Colleges, London, the University laboratories of England, Scotland, and Ireland, as well as those of the Queen's Colleges and of the Royal College of Science in the sister island; to which must be added the laboratories of two institutions of a somewhat different type, viz., Owens College, Manchester, and Anderson's College, in this great city of the north. It is the rapid multiplication of institutions of the Owens College type that constitutes probably the most important feature in the higher intellectual development of the population of this country during the past quarter of a century; indeed, it may very possibly be found in the future that this constitutes the most striking landmark in the history of British intellectual progress during recent times. A glance at the following table will show the remarkably rapid growth of these institutions during the last quarter of the Nineteenth Century:—

Opening of University Colleges.

University College, London		1828
King's College, London		1831
Owens College, Manchester		1851
Durham College of Science, Newcastle		1871
University College, Aberystwyth		1872
Yorkshire College, Leeds		1875
University College, Bristol		1876
University College, Nottingham		1877
Firth College, Sheffield		1879
Mason College, Birmingham		1880
University College, Liverpool		1882
University College, Dundee		1882
University College, Cardiff		1883
University College, Bangor		1884
Finsbury Technical College	} City Guilds.	1883
Central Institution		1885

Thus the opening of the greater number of these institutions falls within the decade 1875—1884.

The benefits arising from the creation of these numerous institutions have not, however, been by any means limited to those persons who have actually taken advantage of their instruction, for their existence has stimulated the establishment of many other institutions, some of which, like the two colleges founded and maintained out of the resources of the City and Guilds of London, although more limited in their scope, afford equal or even greater opportunities for higher scientific training in the particular branches which are represented.

The foundation of these University Colleges and of other institutions for higher education by private initiative, and without a particle of assistance from the public exchequer, is quite in keeping with the history of a country in which it is recognised that the Government does not lead, but only follows where it is drawn or propelled.

It would certainly be anticipated that such a large addition to the machinery for higher scientific training as is represented by the creation of these numerous local colleges during the past twenty-five years would have had a marked influence on the output of scientific discovery in this country. We will endeavour to ascertain whether such a result is discernible in the case of chemical science. Turning to the *Transactions of the Chemical Society*, I have compiled the following table in the hope of obtaining some information on this point:—

*Original Communications in the Transactions of the
Chemical Society.*

1849	..	29	1866	..	47	1883	..	63
1850	..	33	1867	..	49	1884	..	57
1851	..	33	1868	..	47	1885	..	85
1852	..	28	1869	..	37	1886	..	85
1853	..	22	1870	..	38	1887	..	88
1854	..	23	1871	..	28	1888	..	75
1855	..	30	1872	..	32	1889	..	71
1856	..	14	1873	..	46	1890	..	71
1857	..	14	1874	..	49	1891	..	95
1858	..	30	1875	..	49	1892	..	90
1859	..	21	1876	..	54	1893	..	104
1860	..	25	1877	..	58	1894	..	83
1861	..	32	1878	..	61	1895	..	116
1862	..	81	1879	..	84	1896	..	117
1863	..	51	1880	..	75	1897	..	114
1864	..	54	1881	..	75	1898	..	102
1865	..	49	1882	..	65	1899	..	120
						1900	..	127

(The information furnished by these figures was presented in a graphic form by means of a diagram).

The activity displayed in chemical research, as measured by the number of original communications to the Chemical Society, is, however, best followed by a consideration of the aggregate number of papers contributed during the three following decades:—

Decade.	Total number of papers in Transactions of Chemical Society.
1855—1864	352
1865—1874	422
1875—1884	641
1885—1894	847

From these figures it is manifest, even without the application of any of those mathematical processes in which modern chemists are becoming so expert, that the most remarkable increase in the number of original investigations is indeed coincident with that decade, 1875—1884, in which the great majority of the institutions to which I have referred began to throw their prismatic rays of knowledge on many thousands who until then were sitting in shadow or even in darkness.

That these new institutions should have so immediately borne fruit in the manner I have indicated cannot fail to be surprising to those who have been associated with the early years of almost any of these colleges, for when a faithful record of the experiences of their first professors is written the extraordinary obstacles which these pioneers had to encounter, and which in so many cases they successfully overcame, should afford material for a most remarkable, instructive, and even amusing volume. The worthy founders and their executors or trustees appear in general to have supposed that it was only necessary to provide a spacious building, and then appoint a staff of professors who were to do the rest, whilst the necessity of funds for annual upkeep, for libraries, and for assistants was almost overlooked.

It has, indeed, been learnt by bitter experience that the cost of efficiently maintaining institutions of this most ambitious character is enormously greater than was supposed in this country twenty-five years ago, and that founding a college, far from resembling the inauguration of a remunerative business, is very like entrance into the bond of matrimony, with its attendant annually increasing demand upon the pecuniary resources of the paterfamilias.

It would not, indeed, be surprising if some of these modern colleges had been long debarred from contributing directly to the progress of scientific investigation in this country, for this was often assuredly considered amongst the least of the many arduous duties imposed upon their first professors. Ascertained capacity to enrich science was in some cases almost a presumptive disqualification for their chairs, or at any rate took a back seat beside enthusiasm for evening classes and faith in the efficacy of that mysterious panacea "technical instruction." It is indeed

lamentable to think of the valuable years of productive work lost to the country through so much of the energy of these early professors having been sacrificed to these veritable fetiches of our would-be educational reformers.

Notwithstanding the unfavourable conditions under which most of these university colleges had in the first instance to carry on work, it was not long before they showed that they were to become, even during the tenure of office of their first professors, important centres for the prosecution of research—at least as far as chemical science was concerned. Owens College had indeed already led the way in this matter before the period with which I am more especially concerned to-day, for there the first professor of chemistry had pursued his memorable investigations on the organo-metallic compounds, and had, within the first five years after the foundation of the College, enunciated that generalisation which was subsequently extended into the *law of valency*; whilst under his successors, Sir Henry Roscoe, Schorlemmer, Harold Dixon, and Perkin, jun., the Owens College has become perhaps the largest and best equipped school of scientific chemistry in the British Isles.

From the Yorkshire College, Leeds, opened in 1875, there proceeded immediately in rapid succession that whole series of careful investigations relating more especially to specific volume and other physical constants which we associate with its first chemical professor, Thorpe, and his coadjutors.

In the west of England, where the University College of Bristol was opened in 1876, the chair of chemistry was first occupied by the man who has so recently once more proved to the world that there are discoveries made in these islands which for striking originality and independence are unsurpassed and hardly equalled elsewhere. It was during his tenure of the chair at Bristol that Ramsay, assisted by his able fellow-worker and successor Sydney Young, carried out those important and most laborious investigations on vapour pressure and the thermal properties of liquids which not only displayed his extraordinary fertility and resource as an experimenter, but also revealed that exceptional freshness of mind which has enabled him to discern new methods of attacking problems that have already engaged the attention of many able men before him.

Turning from the west of England to the Midlands, where, in 1880, there was founded, through the private munificence of the late Sir Josiah Mason, a college bearing his name, which, before even attaining its majority, was transformed at the psychological moment, as by the wand of the magician, into the University of Birmingham. The first professor of chemistry at the Mason College, my distinguished predecessor Tilden, soon made opportunity there to continue those early researches on the terpenes with which his name will always be associated. We find him also further elaborating the important uses as a reagent of nitrosyl chloride, which he had a number of years previously shown how to prepare in a state of purity, and which has played a somewhat similar part in the exploration of the terpene hydrocarbons that phenylhydrazine has done in the elucidation of the sugar group. In addition to these investigations, we find Tilden at Birmingham also turning his attention to some of the phenomena attending the solution of salts. The younger men attached to the Mason College also found there the opportunity of enriching chemical science with the results of notable investigations; for do we not all remember Thomas Turner's valuable contributions to our knowledge of the influence of chemical composition on the physical and mechanical properties of cast-iron? Whilst early amongst those detailed investigations on the phenomena of solution, which in recent years have had such far-reaching effects on the development of our science, must be mentioned Dr. Nicol's experiments on the volume changes attending the mixture of salt solutions, and on the molecular volume, the boiling-point, and expansion of such solutions.

In the bleak north-east of our island, at Dundee, where a college was founded in 1882 with an extremely handsome endowment by members of the Baxter family, the first professor of chemistry, Carnelley, fired by that restless and almost perfervid energy which doubtless hastened his untimely end, soon found opportunity to interrogate Nature in various directions, notwithstanding the arduous teaching duties which his insatiable love of work had imposed upon himself. Thus, already in 1884, we find him, in his quest for material which should throw light on the periodic relationship of the elements, continuing his laborious work on melting-points and publishing those two ponderous quarto volumes in which every known melting-point was recorded, and forming truly one of the most remarkable compilations ever attempted in our science. Of these volumes he might indeed have said, "*Exegi monumentum ære perennius*," for they will assuredly prove a record of the boundless energy which characterised the man, more imperishable even than the memorial tablet erected by his admiring students and friends in the entrance hall of the Dundee laboratory, which he built and loved so well.

Yet another chemist, whose untimely death we have had to lament during the past twenty years, laboured with marked zeal in one of these new colleges, for it was at Aberystwyth that Humpidge, regardless of his delicate health, and in spite of the altogether unreasonable burden of teaching duties imposed upon him by the terms of his appointment, contributed to our knowledge of the atomic weight of beryllium, and participated in establishing the position occupied by that metal in the natural classification of the elements.

Time does not permit me to further dilate upon the great activity displayed by many of the first occupants of the chairs of chemistry in these provincial University Colleges. It is also unnecessary for me to do more than remind you of the work accomplished by the two Colleges of the City and Guilds of London, the chemical laboratories of which have from their very inception been under the stimulating influences of Dr. Armstrong and Professor Meldola, foci of research from which a number of young chemists of distinction have already emanated.

In recent years we have witnessed the genesis of another class of institution, less ambitious in their aspirations than the University Colleges, but indirectly also of much importance in their bearing upon the nurture of scientific chemistry in this country. I refer to the so-called Polytechnics which have sprung up in several parts of the Metropolis, and to some other institutions of similar scope in different parts of the country. If research in the University Colleges has been the product of their professors rather than of the environment which they afford, assuredly this is even far more so in the case of these Polytechnics, which are primarily evening schools for the benefit of those who have other occupations during the day. That the young lecturers on chemistry at these places should find time and opportunity for original research, and that sometimes of a very high order, is indeed a brilliant testimonial to their indomitable energy, and resourcefulness. Overburdened with large classes until late hours at night, often in those remote and hideous parts of London which suggest to most of us only Slumland, and the philanthropic efforts of Toynbee Hall, or of Dr. Barnardo, these young chemists awake in the morning only to return as rapidly as possible to those laboratories which exercise on them a fascination as subtle and magnetic as that which draws the commonplace Englishman to the golf-links, the cricket-field, or the racecourse. It was in the laboratory of such a technical school, the Heriot Watt College, at Edinburgh, that my distinguished predecessor in this chair, my friend Professor Perkin, created his opportunities for devising and carrying out those now classical methods of building up carbon rings which are the admiration of all organic chemists throughout the world; methods which he has recently brought to such a pitch of perfection that he is not only able to

forgo these rings in great variety, but to "bridge" them with links of carbon atoms. It was at the Heriot Watt College also that his work on berberin was performed, and it was here that he contracted that fertile alliance with Dr. Kipping, his able coadjutor in so many valuable investigations.

At the London Polytechnics, again, more recently, we have had similar examples of fertility, for are we not all familiar with the masterly work of Mr. W. J. Pope, who by his investigations at the Goldsmiths' Institute has extended our knowledge of asymmetric atoms, and has shown that optical activity, which hitherto had only been associated with carbon, and somewhat doubtfully with nitrogen, can certainly be produced, not only by asymmetric pentad nitrogen, but also by tetravalent tin and sulphur? Dr. Hewitt, again, whom I am proud to number among my former students, has shown that the laboratory of the People's Palace, Mile End, may be made a centre in which abstruse investigations on the aromatic compounds can be carried on.

There is, however, perhaps nothing which testifies more strongly to the zeal for original investigation amongst British chemists than the manner in which some of the science masters at our schools have participated in the advancement of chemical knowledge. Some of these schools have, indeed, from time to time secured the services of men whose names are indelibly engraved on the records of scientific chemistry, and it is from the laboratories of these schools that in some cases perhaps their best work has emanated. Of the chemical investigators who have laboured in school laboratories there occur to me, amongst the living, Debus and Clowes at Queenwood, Tilden and Shenstone at Clifton, Purdie at Newcastle-under-Lyme, Brereton Baker at Dulwich, Charles Baker at Shrewsbury. To these names might be added many more; indeed, an examination of the list of Fellows of the Chemical Society shows at what a number of schools throughout the country the chemical teaching is now imparted by men who have themselves advanced the science which they profess.

From the conspicuous instances which I have brought before you—and they might, did time allow, be greatly multiplied—it must be obvious that if a chemist only possesses the necessary enthusiasm and qualifications he will, no matter how inauspicious his surroundings, succeed in doing something to extend the boundaries of his science, and I think I may go further and say without fear of contradiction that in this devotion to research the chemist in this country usually throws into the shade the representatives of other branches of science. How is this pre-eminent zeal of the British chemist to be explained? I believe that there are two principal causes in operation which have brought about this result. Firstly, the great majority of the higher chemical teachers in this country have been trained in Germany, or have been trained by men who were themselves trained there; and secondly, they have only in exceptional cases been educated at the ancient seats of learning. Their inspiration and enthusiasm are almost invariably directly or indirectly traceable to a German origin, and this fire is kept alive by their remaining in constant touch with German chemical literature.

It is being continually impressed upon us in the newspapers, and dinned into our ears from every platform, that it is imperative for this country to approximate more to German ideas and methods, and in general to cast away our insular prejudices, obstinacy, and self-satisfaction. We chemists have already done these things; we have emancipated ourselves from the mischievous illusions which have a tendency to thrive in a country enjoying an isolated geographical position. For, during the last half century the academic springs of Germany have been visited by a stream of young English chemists, a stream which, for the perennial regularity of its flow, reminds one indeed of the pilgrimage made by our fashionable invalids to the same country in the hope of correcting the

effects of high living by the waters of Homburg, Kissingen, and Wiesbaden. There must indeed be few chemists who return from the German temples of science without bringing back at least a spark of the sacred fire to be kindled on an altar at home; and although at times it may be stifled by the island fog, or even burn low through the scarcity of fuel, it generally smoulders long before going out altogether.

The chemist, again, is generally, as I have said, unfettered by an English university record; he stands or falls by the work of his life, and not, as so many others do, by the reputation which they have made in three short years of adolescence at one of the ancient seats of learning.

The spirit of research, which was formerly but a sporadic manifestation within the walls of these venerable institutions, has, however, now become endemic there also, and for a number of years past chemical literature has received a continuous stream of original communications from Oxford and Cambridge, as well as from the Universities of Scotland and Ireland. Instead of those occasional contributions which were customary in the past, we have now evidence that these centres in several cases yield to none in the energy and success with which chemical investigation is being pursued, and that the work of the chemical staff is being shared in by advanced pupils trained at these universities themselves. In this connection it is quite unnecessary for me to remind you of the contributions to British chemistry within recent years by Crum Brown and his pupils at Edinburgh, by Japp at Aberdeen, by Purdie and James Walker at the duplex university now working so harmoniously north and south of the Tay, by Emerson Reynolds at Dublin, and by Harcourt and Harold Dixon, Living and Dewar, Ruhemann, Heycock and Neville, Fenton, Sell, Marsh, and others, who have brought our science into such living prominence on the banks of the Cam and the Isis.

It is, however, not at home only that British chemists have displayed their devotion to research, for with the world-wide relations of the empire it has naturally fallen to the lot of some of our number to carry the science to the uttermost parts of the earth, but it is surely a matter of which we may be justly proud that some of these missionaries, like Mallet, Liversidge, Pedler, and Rennie, have in these distant lands carried out a number of most important scientific investigations; whilst to one of them, Dr. Divers, belongs the great distinction, not only of having carried chemistry to the Far East, but of having reared a most active school of chemical research in that fascinating island empire of the rising sun and the chrysanthemum which has won the unfeigned admiration of the West.

The annals of British chemistry are, however, by no means an exclusive record of the exploits of those engaged in the teaching of our science. I have already referred to the importance of the contributions made by men of leisure, but an equally noteworthy feature of British chemistry is that its progress has been so often furthered by men who have snatched the time for investigation out of a busy professional or industrial life. Belonging to this category the names of a long line of distinguished chemists of our own time suggest themselves:—Warren de la Rue, Hugo Müller, Sir John Lawes, Sir William Crookes, Sir William Abney, Peter Griess, Newlands, O'Sullivan, Horace and Adrian Brown, Harris Morris, Cross and Bevan. To this group of chemists belongs also Dr. Ludwig Mond, whose technical researches have been of such great value to industrial chemistry, whilst his devotion to the pure science is attested by his interesting discovery and investigation of the metallic carbonyl compounds, and by his conception and munificent endowment of the Davy-Faraday Laboratory, in which such unique opportunities for research have been provided by him.

This would appear to be the most fitting moment also to refer to certain other institutions intended for purposes of research which have been established during the past

twenty-five years. Of these the first is the Rothamsted Laboratory, so celebrated during the last half-century for the memorable investigations of Lawes, Gilbert, Pugh, and Warington, but which has more recently, through the generosity of the late Sir John Lawes, been rendered a permanent home for the elucidation of agricultural problems both by laboratory experiments and by trials in the field. Secondly, there is the Research Laboratory which the Pharmaceutical Society has established with the view of raising to a higher level the chemical education of its most promising future members. This laboratory has furnished the opportunity for the valuable investigations of its first director, Professor Dunstan, and of his successor, Dr. Collie. Still more recently a chemical research laboratory has been established in the Imperial Institute. That noble building has within the last few years undergone a process of transverse sub-division, one-half having assumed an independent existence as the nucleus of that still crystallising body, the University of London; whilst in the remaining half the work of the Institute is now carried on in such silence that we have almost forgotten its existence. For where is the flid music with which on summer nights the air of South Kensington was wont to reverberate? Gone. Gone also are the tea-tables, the gardens with their million fairy lights, and the promenading crowds in gay attire. But if the Institute, founded by public subscription to watch over and advance the prosperity of the British dominions, has been impoverished by the discontinuance of these revels, it has become enriched and has gained in dignity by the creation within its walls of a Research Laboratory in which Professor Dunstan and his assistants are busily investigating the chemical nature of numerous interesting products obtained from all parts of Greater Britain.

There can, in my opinion, be no doubt that this much extended cultivation of scientific chemistry in this country, which is such a noticeable feature of the concluding years of the Nineteenth Century, has been greatly assisted by a most fortunate, and more or less accidental, circumstance, without which the energy and enthusiasm of our chemical teachers would have been seriously restricted in their influence. I refer to the very substantial surplus, producing an income of £6000 to £7000 a year, of which the Commissioners of the 1851 Exhibition found themselves possessed, and its utilisation on the advice of the late Lord Playfair for the purpose of the Research Scholarships which have for some ten years past been so highly prized by all the educational institutions permitted to participate in them. The good wrought by these scholarships has been very far-reaching, and it would be difficult to praise too highly the wisdom displayed by the Commissioners in drawing up the conditions on which they are awarded. Firstly, by not limiting them to any one science, they have stimulated a wholesome rivalry between departments to bring on their promising students to the level of scientific investigation. Secondly, they have compelled the governing bodies of educational institutions to recognise and make provision for research as part of the regular programme of these places. Thirdly, they have encouraged talented students to devote an additional year, or even more, to their education in the hope of securing one of these prizes; and these students have thus provided their teachers with the *personnel* necessary for carrying on scientific work. Fourthly, the scholars themselves have had the inestimable advantage of extending their horizon, and of coming in contact with other teachers, other schools of thought, and other views of life. Fifthly, these scholars on their return, and before they have obtained definite employment, are welcomed as supernumeraries in English colleges, where they have an opportunity of continuing their researches, and where they assist in imbuing the students with the spirit which they have themselves imbibed. Lastly, these and other scholarships of a similar character are providing the country with a body of highly trained men whose value to the nation is annually becoming more appreciated, and whose work will con-

tinue to bear fruit directly or indirectly for an indefinite period of time. These Exhibition scholarships have now been awarded since 1891, and already no fewer than sixty-five chemists, including three women, have enjoyed the enormous privilege of extending their education for a period of two, and in special cases even three, years under the most favourable surroundings.

Bearing in mind the rooted objection which pervades the people of this country to expend any public money on higher education, it is marvellous that it should have been possible to employ this fund, which after all is of a quasi-public character, for what may be described as educational use at a high potential, instead of its being dissipated in the manner so dear to Englishmen, by benefiting to an infinitesimal extent a much larger number of persons. Indeed, but for the vertebrate character of the Commissioners in 1877, the fund would have been thus frittered away, for in that year they were waited upon by a deputation of influential persons who urged that the money should be distributed in grants to provincial museums. Had that been done what would have been the result? The masses would have had a few more glass cases to gaze at on wet days and bank holidays!

There can, I think, be little doubt that in this matter of the allocation of funds intended for the public good we have reached a turning-point in the road which we have been so long pursuing. Until recently it has been the feeling of a very powerful majority in this country that public money should only be spent in such a way as to directly benefit very large numbers; and in the case of educational funds, therefore, it was only their utilisation for the benefit of the masses that could be entertained. Now, whilst it is indubitable that the improvement of our primary education was for many years a crying necessity, it has long been obvious to a minority that this policy is systematically starving that higher education in which we are lagging more and more behind those other countries in which greater elasticity prevails, and in which the immediate and obvious wants of the community receive prompt attention without regard to the traditions and doctrinaire principles of a past generation. In the matter of higher scientific education, at any rate, it is becoming more and more widely recognised that its starvation through attention being exclusively directed to the low-level education of the masses is defeating the very ends which this policy has in view. Indeed, some practical men, and even a few statesmen, realise that the many are beginning to suffer from the results which this policy has had on our manufactures and commerce, without which the multitude can have no existence at all.

The more than princely patronage of higher education by that Scotsman who has not forgotten the land of his birth during fifty years spent in a country which has afforded the necessary scope for his genius and energies, illustrates the change in the wind of opinion amongst practical men; for Mr. Andrew Carnegie's handsome contribution to the funds of the University of Birmingham, and his endowment of the universities of Scotland on a scale which is altogether without precedent, clearly show which, in his opinion, are the rungs in the educational ladder of this country that require strengthening in the interest of those very masses which it is his earnest desire to benefit. The still more recent response of the City Council of Birmingham to Mr. Chamberlain's suggestion that a rate should be levied in aid of the university of that city is further evidence that Mr. Carnegie's practically expressed opinion is shared by the enlightened rulers of that great municipality to which I have the privilege of belonging.

These, ladies and gentlemen, are, I believe, no mere sporadic manifestations, but unquestionably signs of the times. The opening of the new century is in reality a year of very serious awakening to those Englishmen who are not deaf to the voices in the air around them. It is rapidly dawning upon many that "the greatest empire which the world has ever seen" cannot be maintained

unless we cast off insular prejudices and traditions, and make a careful study of those points in which other nations are our superiors, with a view to the intelligent adaptation and development, as distinguished from mere imitation, of their methods to our own particular needs.

The survey of the British chemical world at the dawn of the Twentieth Century affords, however, scope for satisfaction in many ways. Not only have the places in which higher chemical work can be and actually is carried on been greatly multiplied, but the number of workers has been largely increased; and although the enthusiasm of these workers cannot well be greater than that of those who laboured so successfully twenty years and more ago, it has not become diminished, and is certainly diffused more widely amongst the *personnel* of our colleges and universities. In this connection I need only remind you of the large number of active and independent investigators who are to be found amongst the members of the junior staff at almost every college in the country, and which is altogether without parallel in the past.

There are hardly any of the great problems now exercising the minds of chemists throughout the world which are not being worked at by some of our number; whilst that some chapters in the recent progress of chemical science are more or less specifically British, I would only remind you of the isolated labours of Dr. Perkin in the field of magnetic rotatory power; of Sir William Crookes's exploration of the phenomena occurring in high vacua; of the researches of Abney, Russell, and Hartley on the absorption spectra of organic compounds; of the investigations by Harold Dixon and Brereton Baker of the behaviour of substances in the complete absence of moisture; of the extension by Pope and Smiles of our knowledge of asymmetric atoms; of the near approach to the absolute zero of temperature by Dewar; and of those marvellous discoveries of Rayleigh and Ramsay which have not only introduced us to five new aerial elements, but have revealed the existence of a hitherto unknown type of matter, which is apparently incapable of entering into chemical combination at all.

But whilst we may thus congratulate ourselves on this increased activity in chemical investigation, and upon the maintenance of a high standard of quality by the exceptional brilliancy of the researches of some of our number, we must now carefully consider how we stand with regard to the absolute quantity of our output.

I have called your attention to the evidence of activity in the British chemical world which is furnished by the number of original investigations communicated to the Chemical Society of London. Let me now ask you to turn to the corresponding picture, which is furnished by the statistics of the much younger Chemical Society of Berlin.

Original Communications to the Chemical Society of Berlin.

1868	..	97	1879	..	604	1890	..	630
1869	..	252	1880	..	563	1891	..	677
1870	..	277	1881	..	495	1892	..	553
1871	..	288	1882	..	541	1893	..	587
1872	..	303	1883	..	535	1894	..	653
1873	..	420	1884	..	646	1895	..	636
1874	..	516	1885	..	686	1896	..	566
1875	..	488	1886	..	696	1897	..	560
1876	..	517	1887	..	708	1898	..	555
1877	..	568	1888	..	658	1899	..	549
1878	..	602	1889	..	601	1900	..	636

A comparison between these figures and those of the London Chemical Society is best effected by means of a diagram, which speaks for itself, and shows that chemical science occupies an entirely different place in Germany from that which it even now does in this country. The curves in this diagram bear, indeed, somewhat the same relationship to each other as do the homely elevations of the Grampians to the snow-clad peaks of the Andes.

Is this state of affairs to continue throughout the Twentieth Century? Are intellectual ambitions to be for

ever subordinated to the extension of territory, to the acquisition of that metal which has had its atomic weight so accurately determined by Thorpe and Laurie, and to those other problems which fill the political horizon? Even the most recent awakening of interest in higher scientific education is not altogether of the breed to satisfy us as men of science; for the interest is assuredly not in the pursuit of knowledge for its own sake, but is aroused by the desire to secure those material advantages which it is beginning to be realised must inevitably result from the steadfast prosecution of scientific research. This is indeed a very different spirit from that which has led to the proud position occupied by science and learning of all kinds in Germany.

Schiller has truly said—

“Knowledge is to one a goddess, to another only an excellent cow.”

I fear there can be no doubt that here it is the cow, and not the goddess, that is in request. Thus, whilst in Germany the love and reverence for knowledge preceded the esteem of knowledge for the material benefits which it confers, we must hope that in our country the eagerness to secure the material advantages will perhaps lead to a love and reverence for that which confers them, so that in the course of time, perhaps, the useful cow will be allotted a stall on Olympus, or be at least pastured on the grass of Parnassus.

From whatever motive, whether utilitarian or otherwise, we wish to see the position of science in this country raised, and the qualitative and quantitative output of scientific work increased, I imagine that the methods to be immediately pursued for attaining this end must be very similar.

If the higher teaching of science is to be really encouraged the first necessity is that this higher teaching shall offer a sufficiently attractive career to the man of ambition as well as to the enthusiast. We all know that the supply of enthusiasts of intellectual power combined with capacity to perform is extremely limited and wholly inadequate for carrying out the important work of the world, and that the greater part of such work is actually done by men of ambition.

In order that the academic world may attract the ablest men of ambition as well as that *rara avis*, the able enthusiast, it is necessary that the highest prizes for academic distinction should carry similar social prestige, similar remuneration, and similar opportunities of exerting public influence as are enjoyed by the leaders of other professional callings; they should be at least equal to those of the Archbishop of Canterbury or of the Lord Chancellor. It is not by any means necessary that such prizes should be numerous, as is abundantly demonstrated by the volume of able ambition which is drawn into the Church and to the Bar by the comparatively few opportunities for great success in those professions. The enthusiasts already find their way into the academic world; and, although they maintain the quality of British scientific work, they are unable, by virtue of their scarcity, to maintain the quantity which is essential for the luxuriant growth of science in our midst, whilst the absence of such tangible rewards as are bestowed in other spheres of intellectual activity prevent the importance of science being recognised by a public which has no appreciation of the inward and spiritual grace unless guided by the outward and visible sign.

Precisely the opposite policy, as far as remuneration is concerned, has, however, been pursued in the academic world during recent years, the few very moderate prizes which formerly existed having been deliberately commandeered to more nearly equalise the value of the chairs in all departments.

The principle of equalising the remuneration of different chairs is as inequitable as it is utterly unsound from a business point of view. The principle is unsound because equal salaries will not secure men of similar standing in different subjects, it is inequitable because the amount of

work attaching to the chairs of different subjects is necessarily very unequal, as is the order of intellect required for the successful discharge of their duties.

Again, the system which is gaining ground in this country of allocating a certain stipend to a chair is unbusinesslike and mischievous. It is as irrational to fix the remuneration of a particular chair as it would be to fix the price to be paid for one's portrait, irrespectively of whether it were taken by a photographer or painted by a Royal Academician. If we really want the best man for any particular professional service, whether it be to treat us for a disease, to plead our cause in a court of law, or to perform on some musical instrument for our delectation, we know we must make up our minds to pay the price which the best man commands in his particular profession, and it is absurd to suppose that the same principle does not hold good in the matter of securing the best man for an academic appointment. This, again, is intimately connected with the desirability of providing a sufficient number of steps in the academic ladder, so that it shall not be possible for the “young man of promise” to be rushed into a first-class appointment from which he has no ambition to move for the remainder of his days.

Another matter, again, requires consideration; if we are really in earnest in the attempt to bring our universities abreast of those in other countries, our chairs must be systematically thrown open to the whole world, and the best men obtainable secured, irrespectively of their nationality. Not only have small nations adopted this plan, but even the nation which is pre-eminent for its academic strength is by no means blind to the importance of drawing into its service from the outside men of commanding brilliance and power. I need not remind you that England has also exhibited a wise and liberal spirit in this matter in the past, and that, as far as our science is concerned, this policy has been most fully justified. For, consider only what the English Chemistry of the latter half of the Nineteenth Century owes to the genius and magnetic influence of the imported Hofmann. I can imagine the electors to British chairs suggesting that there might be linguistic difficulties in the way of carrying out such a policy, in answer to which I would appeal to the pupils of Hofmann to say whether his stimulating discourse lost anything of its vigour and inspiration through the strong Hessian accent with which every word of it was saturated. It is to be hoped that no narrow and short-sighted policy, disguised under that too often mis-used word “patriotism,” will seek to close the doors of our universities to the genius and ability of other nationalities.

I believe, however, that one of the most urgent and pressing of University reforms is that greater facilities should be afforded for the migration of students from one university to another, without prejudice to their acquisition of a degree. It is the present system, which practically chains an undergraduate with links of steel to the university at which he matriculates, that is at the root of many of the evils under which our higher education is labouring.

The university at which a youth matriculates is often determined by the fatuous, although pathetic, wish of the father that his son should spend his time, I will not say work, amidst the surroundings which awaken such pleasant memories in himself; and the youth once within the magic portals has little or no opportunity of rectifying the possible mistake of his fond parent, who has probably for a quarter of a century been quite out of touch with university matters, or even divorced from the intellectual world altogether.

This foolish sentiment of loyalty to a university or even college is sometimes kept up for generations, and I have met persons who have told me that their family had always been Balliol or Trinity men, with the same sort of pride that they would doubtless have informed me, had they been able, that their ancestors came over with the Conqueror, or had charged with the Cavaliers at Naseby.

The prevalence of such a sentiment shows that our

universities are principally valued for their social attractions, as well as for their past history and ancient traditions, in which connection it is always well to remember that a living dog is better than a dead lion.

The possibility of students dissociating themselves from the university of their matriculation and freely migrating from one school to another would, in my opinion, not only be of immense advantage to the students themselves, enabling them to obtain the best instruction in each particular subject, and greatly extending their horizon and knowledge of the world, but it would operate most favourably on the universities themselves, minimising the tendency to stagnation, and compelling those who hold the purse-strings to provide for the strengthening of weak departments. Nor should the possibilities of migration be limited to the Universities of the United Kingdom, or even of the British Empire, but the prospect should be kept in view of ultimately effecting an arrangement whereby students could enjoy the advantage of visiting the universities of other countries.

Such migration is, of course, closely connected with the duration of the period of university study, and in this matter reform is most urgently needed. The traditional three years devoted to the acquisition of a degree is hopelessly inadequate for the higher purposes of university training, especially when the very immature age at which English students generally begin their university career is taken into consideration. The period of academic study should be forthwith extended to five years, as it is only in this way that the university can be effectively made a centre of research. Without a course of study of such duration, and of which research forms a part, it is quite impossible that the highly trained men who are now so urgently needed for practical avocations should be produced.

In this connection, again, we all know that much mischief has been going on in recent years. Instead of the terms on which degrees are at present obtainable being regarded as too lenient and easy, proposals are actually being put forward in some quarters to enable persons attending evening classes to thereby qualify for university degrees. Now, whilst it is of the utmost importance to provide abundant opportunities for the talented poor to obtain a university education by reducing the fees, and by instituting a sufficient number of bursaries, it is imperative that those who are to be stamped with the distinctive mark of a university should have devoted their whole and undivided attention, over a certain period of time, to the courses of study prescribed. Let us beware of introducing the half-time system into the university, a system which we know to be a deplorable makeshift even in the elementary school.

In this matter of the aspirations, scope, and functions of a university we have not merely to contend with the ignorance and apathy of the average Philistine, but we are wrestling against principalities, against powers, and against darkness in high places. Thus, only four months ago one of our most prominent statesmen, whose oracular and sporadic utterances inspire amongst millions almost the awe and respect which is felt for the supernatural, is reported in the columns of the daily papers to have said at one of the most important educational gatherings of this first year of the new century:—"You, Mr. Vice-Chancellor, spoke of the stigma that would rest on the University if it did not annually produce some work of original research. I, from another point of view, am contented if you do nothing of the kind. I am satisfied to think that in a large and increasing degree you will train men and women fit for the manifold requirements of this Empire." This statesman, who it is not surprising to find was educated at Eton and Oxford, is thus of the opinion to-day, unless, indeed, his views have changed in the interim, that it is possible to train men and women fit for the manifold requirements of this Empire without bringing, at any rate, some of them into contact with the living spirit of research—that spirit which, operating through the

ages, has enabled man to transform the wilderness in which he was placed by his Creator into the garden of material and intellectual enjoyments in which that statesman was himself born.

I would ask you to contrast with the views of the distinguished *alumnus* of Eton and Oxford the utterance of another statesman who, unhampered by such educational antecedents, has formulated the following ideal for the guidance of that university which he has himself created:—

"The third feature to which I should call attention, and which, I am inclined to say, is of all the most important, is that a university should be a place where knowledge is increased, and where the limits of learning are extended. Original research, the addition of something to the total sum of human knowledge, must always be an essential part of our proposals."

Lastly, we have to consider whether this university work, in which we hope for such great developments in the Twentieth Century, is still to be carried on by what is virtually private enterprise and private endowment, or whether it is to be provided for by taxation.

If the reforms and developments which are being preached from so many platforms are to be really carried out, if even our higher scientific training alone is to be brought into line with that which is provided in many other countries, it is indubitable that expenditure will have to be enormously increased. Now, profoundly as we all admire the enlightened public spirit of the men and women who have in the past endeavoured out of their private resources to help forward the great movement of higher education, it is, I believe, the firm conviction of all who have any real knowledge of what this higher education means, and a clear conception of what must be done in order to put it on a proper footing in this country, that on private benefaction alone this work cannot be accomplished. But even if private endowment could raise this great edifice in our midst, it is obvious that we should have to wait indefinitely for its realisation. Voluntary contributions cannot be made to come at the bidding of those who stand in need, nor directed into the channels where they will produce the most good; they have to be patiently waited for, with the result that valuable time is lost and opportunities pass by never to return. Private benefaction, moreover, is almost always retrospective; a hospital is not founded by the charitable until the sick are dying unattended; almshouses and orphanages are not thought of until the widow and the fatherless are either starving in the streets, or begging on the doorstep. What we so forcibly recognise in this matter, however, is that we have not only to make up for leeway in the past, but that we must now exercise prevision to prevent similar disastrous lapses in the future. The state of affairs to which we have been reduced must not be allowed to occur again; the warnings of those possessing special knowledge in these matters must not be disregarded in the future as they have been in the past, for it is no exaggeration that the whole of the learned societies and academic bodies of this country put together have at present a smaller corporate share of political influence than a Temperance League or a Trades Union. To what has this state of things reduced us? The humiliating spectacle of "the greatest Empire the world has ever seen" at the beginning of the Twentieth Century without a teaching university in its Metropolis, and engaged upon the task of tardily patching one together out of those heterogeneous elements of uncertain valency which are to hand. Is the completion of this structure, on a scale challenging comparison with the universities which are to be found in the other great capitals of Europe, to be delayed until a millionaire, or rather series of millionaires, can be induced to finance it? To this work, and to other works like it, is it not fitting that every inhabitant of this country should contribute? For these are works which assuredly benefit all classes, not only of this generation, but of those which are to come—at least as much as the acquisition of territory at a distance of 8000 miles from home, and for which

purpose the nation is apparently willing to pay at the rate of one and a quarter million sterling per week for an indefinite period of time.

It is sometimes urged that this higher education does not benefit the masses; but could any contention be more erroneous? The poor have really a far greater stake in the prosperity of our home industries and commerce than the rich; for whilst the decay of our producing power will remove the very means of subsistence from the poor, it matters very little to many of the rich whether their dividends are derived from home-enterprises or from those of a Billion Dollar Combine, or some similar transatlantic Trust or Corporation.

Higher education and true universities are also amongst the most potent factors in breaking down the hereditary stratification of society, and in minimising the advantages depending upon the accident of birth, so that, with the greatly enhanced facilities which must be provided for students without means, they should afford in the future, even more than they have done in the past, an avenue for the humblest boy of talent to that position which he is by natural endowment and by his own exertion best fitted to fill in the interests of the State.

Is this great work of raising up a worthy system of national higher education, and of creating a living interest and widely diffused enthusiasm for knowledge, and for the increase of knowledge in all its branches, going to be accomplished during the century of which we have but crossed the threshold? Even the most sanguine among us dare not unhesitating say yes; but assuredly upon the answer, which is hidden by the veil of the inscrutable future, depends in the very highest degree, not only the material and intellectual welfare of the rising generations, but also the good name and reputation of the Empire in our own time, and the gratitude which, above all things, we should strive to earn from that immortal part of us which we call Posterity.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, September 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month was 2.12 inches, the average fall being 2.38 inches; this leaves a deficit of 0.26 inch, and raises the total deficit for the year to 0.39 inch, or 2.5 per cent on the thirty-five years' average.

Our bacteriological examinations of 545 samples have given the results recorded in the following table; we have also examined 39 other samples, from special stand-pipes, &c., making a total of 584 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	284
New River, filtered (mean of 130 samples) ..	13
Thames, unfiltered (mean of 26 samples) ..	1646
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 299 samples) ..	22
Ditto ditto highest	280
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	223
River Lea, from the East London Company's clear-water wells (mean of 38 samples) ..	16

Of the 467 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 22 samples, or 4.7 per cent, were sterile. Five samples contained more than 150 microbes, and six samples, or 1.2 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the six excess samples was 212, against a corresponding mean of 173 in the 31 excess samples of July.

These figures show that the London Water Supply is quite on a level with its normal high standard of excellence.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 134).

G. The Influence of the Nitrous Acid contained in the Nitric Acid on the Stability of Gun-cotton.

IN the industry of the nitroglycerin and nitrocellulose explosives, the idea prevails that the presence of nitrous acid in the nitration mixtures tends to diminish the yield as well as the stability of the products generated.

There was to be found only a single research published on this point, and this, dating from year 1847, was by Payen. This experimenter states that nitrous acid diminishes the yield as well as the proportion of nitrogen in the nitrocellulose. Apparently no fresh research was undertaken in this connection for more than fifty years.

It is certainly not improbable that the action of nitrous acid diminishes the stability. In the nitration mixtures of nitric acid and concentrated sulphuric acid used in the manufacture of gun-cotton, the greater part of the nitrous acid must be present as nitrosyl-sulphuric acid. But as the reaction $\text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{SO}_2\text{NH} + \text{HNO}_3$ is reversible, there is always to some extent some free nitrous acid present.

This circumstance is of great practical importance, for if the nitrous acid should indeed exert the injurious influence, as is supposed, the manufacture of nitric acid must be conducted with greater care than heretofore. But there were always experimenters who were of opinion that the nitrous acid was by no means injurious, and it seemed advisable to resume the research carried out half a century ago, which was therefore started a few years ago in this laboratory.

Lunge and Weintraub state that with less than 6.5 per cent nitrous acid in the nitric acid (which in practice is the maximum amount present), the N_2O_4 exerts no appreciable influence. A small difference was only noticeable

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

when the nitrous acid rose to 12 per cent, the nitrogen of the gun-cotton then sinking to 210.78 c.c. The stability of the products was not then tested. It therefore remained for us to proceed with stability relationships.

It is not yet clear as to which is the most reliable test of stability. In order to decide which was best suited to our purpose, we had next to make comparisons between the different methods.

In their underlying causes and actions, the stability relationships of gun-cotton are so far insufficiently known to us. Hence it happens that the methods adopted for its examination are more or less empirical, and afford no absolute values.

The measure of stability usually taken is the time during which a certain quantity of the explosive can be maintained at a certain temperature till the first trace of decomposition sets in. This shows itself in the production of nitric acid, which is detected by an indicator. The universal "heat test" of Abel is based upon this principle. Potassium iodide is used as indicator in this case.

As this reaction may be obscured by certain by-products of the explosive, Osk. Guttmann substituted a new reagent, viz., diphenylamine. At the beginning of the reaction, a yellow zone is first formed on the moistened part of the test-paper, and after one to two minutes a blue band should suddenly appear on the dividing line between damp and dry. But, according to Thomas, this blue colouration established itself quite gradually; and we ourselves, after numerous determinations, could not get the sudden appearance of the blue line. Shortly after the production of the greenish yellow zone, a bluish tinge was visible, which became intensified in the course of a few minutes. By taking as a standard a certain degree of intensity of the blue colour, sufficiently accurate results may be obtained by this method.

On the other hand, Spica rejects the diphenylamine test, neither could he confirm the sudden appearance of the blue zone. Hence, Spica proposes another reagent, viz., metaphenyldiamine, which is said to be considerably more sensitive than the other. We rather doubt that this is of any advantage. As this part of our work was already concluded before the appearance of Spica's results, we carried out no determinations with this method.

The material used in these experiments had necessarily to correspond in stability to practical requirements. Hence it had next to be determined how to attain this in the production of gun-cotton on the small scale. This question stands in intimate relation with that of the cause of instability. Formerly the latter was attributed entirely to residual traces of the nitration acids; and hence it would be only necessary to remove the latter by washing. The once frequent explosions in gun-cotton factories have thoroughly proved that stability is not to be obtained by lengthened washing in cold water, or even in running water; and Abel's method is now universally adopted, in which the nitration products are pulverised and washed with boiling water.

(To be continued).

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 103).

Lunge-Trillich or Seyler Method.

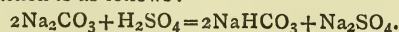
THIS method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid, and of carbonates and bicarbonates of the alkaline earth bases; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

Leeds (*Journ. Amer. Chem. Soc.*, 1891, xiii., 98), in this

country, and Trillich in Europe, proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralised, any further addition of sodium carbonate produces a pink colour. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to the assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of this "phenolphthalein alkalinity," and the "total alkalinity" obtained with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course free carbonic acid is absent.

Seyler, who has made a study of this method, considers it one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that, when a water was acid or neutral to phenolphthalein, there was present for each molecule of fixed carbonic acid, one molecule of half-bound carbonic acid; and to the claim that when the water was alkaline to phenolphthalein, only one-half the carbonic acid in the form of the normal carbonates was determined by titrating with acid to the discharge of the colour produced by this indicator.

If to 10 c.c. of a cold 0.02 normal solution of sodium carbonate, phenolphthalein be added, and then a 0.02 normal solution of sulphuric acid, it will be found that only 5 c.c. of the latter are required to discharge the colour. The reaction is as follows:—



The pink colour produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid; and this occurs when one-half the base has been neutralised. It is therefore evident that bicarbonates of the fixed alkalis are neutral to phenolphthalein.

The assumption that carbonates of the alkaline earth bases react in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

A calcium bicarbonate solution was boiled down to about one-third or one-fourth of its original volume, and allowed to cool out of contact with the air. The precipitated calcium carbonate settled out, only such remaining in solution as was soluble without the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn, and titrated with acid, using phenolphthalein as the indicator. The total alkalinity of the solution was also determined with the indicator lacmoid.

Action of Phenolphthalein as an Indicator in a Solution of Calcium Carbonate.

No.	Calcium carbonate solution.	Sulphuric acid.	Sulphuric acid.
		N/50 (approx.).	N/50 (approx.).
		A.*	B.†
	C.c.	C.c.	C.c.
1	100	1.65	3.15
2	100	1.65	3.25
3	100	1.50	3.10
Average		1.60	3.17

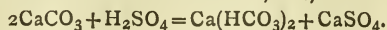
* To discharge pink colour with phenolphthalein.

† To obtain end-point with lacmoid.

A solution of magnesium carbonate acted similarly, 1.65 c.c. of acid being required to discharge the pink colour formed with phenolphthalein, and 3.4 c.c. to obtain the end-point with lacmoid. The reaction involved in these

* *Journal of the American Chemical Society*, xxiii., No. 6.

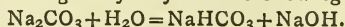
two cases is doubtless analogous to the one which takes place in sodium carbonate solutions, viz.,



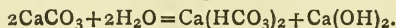
It was found that these solutions of calcium and magnesium carbonate were very sensitive to the absorption of carbon dioxide from the air, even on a very short exposure; and also that it was extremely difficult to free them from the last traces of the half-bound carbonic acid. Only by violent and prolonged boiling and cooling out of contact with the air could this be accomplished. A calcium carbonate solution, which after boiling was cooled in air free from carbon dioxide, required for 100 c.c., 1.5 c.c. of acid with phenolphthalein as the indicator, and 3.1 c.c. with lacmoid. A portion of the same liquid cooled in a beaker required 0.95 c.c. of acid with phenolphthalein, and 3.2 c.c. with lacmoid. Magnesium carbonate solutions absorbed carbon dioxide more slowly, as has been previously pointed out.

Hot solutions of calcium carbonate and of magnesium carbonate do not react to phenolphthalein in the same manner as do these cold solutions, since in the former the bicarbonates formed by the liberation of the carbonic acid from the normal carbonates are immediately decomposed by the heat with evolution of carbon dioxide. It is therefore possible to determine the whole of the carbonates of the alkaline earth bases even with phenolphthalein as the indicator, provided the solution is kept boiling. The same is true of the carbonates of sodium and potassium. But phenolphthalein is by no means a good indicator for this purpose, and the results are much more accurately obtained with lacmoid or one of a similar character.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner:—



As the sodium bicarbonate thus formed supplies no hydrogen ions, and the sodium hydroxide is dissociated, producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.



If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein, and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

(To be continued).

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A SUMMARY).

By HARRY C. JONES.

(Continued from p. 136).

Organic Solvents (continued).

Pyridine.—Our knowledge of the dissociating power of pyridine we owe almost entirely to St. v. Laszczynski and St. v. Gorski (*Zeit. Elek. Chem.*, iv., 290). They measured the conductivities of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium, and ammonium sulphocyanates in pyridine, over a wide range of dilutions. A few of their results are given:—

Potassium iodide.		Sodium sulphocyanate.	
v.	μv.	v.	μv.
178.49	22.04	32.24	7.98
713.9	30.68	128.96	12.79
2855.6	38.05	515.84	20.56

The conductivities are very considerable in this solvent.

* *American Chemical Journal*, xxv., No. 3.

Werner (*Zeit. Anorg. Chem.*, xv., I., 39), found that certain inorganic salts in pyridine conduct very well, and yet show little or no dissociation by the boiling-point method.

Other Organic Solvents.—A few measurements of the conductivity of one or more substances in a number of solvents have been made, but the work with any one of the remaining solvents is so slight that it does not call for special treatment. Thus, Werner (*Zeit. Anorg. Chem.*, xv., I., 39), found that cuprous chloride in ethyl sulphide conducts very poorly. Cattaneo (*Biebl. Wied. Ann.*, xvii., 365), studied a few solutions in glycerin, and found that they had larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Kablukoff (*Zeit. Phys. Chem.*, iv., 429), measured the conductivity of hydrochloric acid in benzene, xylene, and hexane, and showed that solutions in the hydrocarbons conduct very poorly.

Dutoit and Aston (*Comptes Rendus*, cxxv., 240), measured the conductivity of electrolytes in benzene chloride, ethyl iodide, ethyl bromide, and amyl acetate, and found that solutions in these solvents conducted very poorly. They found, on the other hand, that solutions in nitroethane conduct very well. Dutoit and Friderich (*Bull. Soc. Chim.*, [3], xix., 325), worked with acetophenone as solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate as electrolytes. The conductivity in this solvent was small.

Four other solvents have thus far been studied—ethyl acetate, ethyl acetoacetate, benzaldehyde, and nitrobenzene. This work has been done by Kahlenberg and Lincoln (*Journ. Phys. Chem.*, iii., 12). As electrolytes they used ferric and stannous chlorides, bismuth trichloride, and antimony trichloride. The conductivities in these solvents are, in general, small, but vary considerably with the nature of the electrolytes used.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

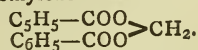
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 7, August 12, 1901.

The Colour of Ions.—G. Vaillant.—The author performs a series of experiments on the absorption spectra of solutions of permanganates of potassium, barium, and zinc, and he verifies the following statements. (1). In completely dissociated solutions, only containing one coloured ion, the colouration is independent of the nature of the other ion. (2). If, on the contrary, ionisation is incomplete, the colouration varies with the nature and the concentration of the colourless ion. (3). The colouration of a solution of any concentration whatsoever is usually connected with its degree of dissociation, and this connection is expressed by a formula of two variables and two only, one characterising the complete molecule and the other the dissociated molecule.

The Value of Molecular Weights at the Temperature of Ebullition.—M. de Forcrand.—Some months ago the author stated the following general law. "In all chemical or physical phenomena the heat of solidification of a molecule of any gas whatsoever is proportional to the absolute temperature of ebullition under atmospheric pressure." He now notices one of the consequences of this general relation, by examining bromine, iodine, mercury, nitric acid, and nitric anhydride, and finds, particularly from a study of the last example, a remarkable agreement existing between the results now obtained and those already published. His researches on the properties of the above examples allow of the calculation of the rela-

tion between the molecular weight (M) and the temperature (T).

Action of Benzoyl Chloride on Trioxymethylene in presence of Zinc Chloride.—Marcel Descudé.—In a preceding research the author showed that zinc chloride considerably facilitates the union of acetyl chloride with the methylic and ethylic aldehydes. By the action of benzoyl chloride on trioxymethylene, he prepared a compound corresponding to the formula $C_{14}H_{12}O_4$. He discovered since that this formula is inexact and ought to be replaced by the following, $C_{15}H_{12}O_4$, which represents the composition of methylene dibenzoate—



He now attempts to combine directly benzoic anhydride and methanal, and prepares methylene dibenzoate by this method in a pure crystalline state. These crystals are doubly refracting and melt at 99° to a colourless limpid liquid, which boils at 255° .

No. 8, August 19, 1901.

Researches on the Mechanism of Etherification in Plants.—E. Charabot and A. Hébert.—The authors believe that in plants etherification is produced by the direct action of acids on alcohols; this is favoured by a particular agent which plays the part of dehydrator. Various experiments were made on the terpenic compounds and the following conclusions drawn. (1). Under the pure and simple action of acetic acid, linalol is etherified with extreme slowness, only in plants. (2). Terpenic alcohols, which under the influence of an acid are etherified more easily, are also those which vegetables contain in the largest proportion combined with the same acid. (3). For the same terpenic alcohol, the acid combining the most easily with this alcohol is that whose ether is the most abundant in the plant. (4). When two alcohols co-exist in a vegetable, if these two alcohols are etherified, the acid divides itself between them in the same proportion as they are present in the plant.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Glasgow Meeting of the British Association:—

President—Prof. Percy F. Frankland, F.R.S.

Vice-Presidents—Dr. E. Divers, F.R.S.; Prof. J. Ferguson, LL.D., F.R.S.E.; Prof. W. H. Perkin, F.R.S.; Prof. James Walker, F.R.S.; Dr. T. E. Thorpe, F.R.S.; Dr. W. A. Tilden, F.R.S.; Prof. A. Michael; Prof. E. W. Morley.

Secretaries—Dr. W. C. Anderson, M.A.; Dr. G. G. Henderson, M.A.; Prof. F. S. Kipping, F.R.S.; Prof. W. J. Pope; Dr. T. K. Rose (Recorder).

Committee—Sir W. Roberts-Austen, LL.D., F.R.S.; G. T. Beilby; C. H. Bothamley; Adrian Brown; Prof. Campbell-Brown; Prof. Dobbie; Prof. H. B. Dixon, F.R.S.; Prof. W. R. Dunstan, F.R.S.; Prof. J. Gibson; Dr. J. H. Gladstone, F.R.S.; Dr. A. G. Green; Dr. W. T. Lawrence; Prof. Hartley, F.R.S.; Dr. E. A. Letts; Prof. Willy Marckwald; Dr. Forster Morley; Prof. H. M'Leod, F.R.S.; Dr. W. H. Perkin, sen., F.R.S.; Prof. T. Purdie, F.R.S.; Prof. W. Ramsay, F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; Prof. J. Sakurai, LL.D.; Dr. M. W. Travers; Prof. J. M. Thomson, F.R.S.; Prof. Paul Walden.

The Papers brought before the Section were as follows:—

President's Address—The Position of British Chemistry at the Dawn of the Twentieth Century.

Dr. W. T. Lawrence—Duty Free Alcohol. (Followed by a Discussion).

Dr. A. G. Green—The Coal Tar Industry.

Report of the Committee on preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Prof. Adrian Brown—Enzyme Action.

Prof. W. Marckwald—Radium.

Report of the Committee on the Relation between the Absorption Spectra and Chemical Constitution of Organic Substances.

Prof. E. A. Letts—Chemical Changes during Contact of Sewage with Bacteria.

Dr. S. Rideal—Humus and the Irreducible Residue in the Bacterial Treatment of Sewage.

Dr. S. Rideal—Sulphuric Acid as a Typhoid Disinfectant.

W. Thomson—Arsenic in Beer.

W. Ackroyd—Inverse Relation of Chlorine to Rainfall.

W. Ackroyd—The Distribution of Chlorine in Yorkshire.

Dr. J. H. Gladstone and G. Gladstone—Hydration of Tin, including the Action of Light.

Dr. J. H. Gladstone and J. Hibbert—Transitional Forms between Colloids and Crystalloids.

Report of the Committee on the Nature of Alloys.

G. T. Beilby—Minute Structure of Metals.

Prof. A. Michael—On the Three Stereomeric Cinnamic Acids.

Prof. A. Michael—On the Genesis of Matter.

Prof. A. Michael—On the Process of Substitution.

Prof. W. H. Perkin, F.R.S.—On the Synthetical Formation of Bridged Rings.

Prof. G. G. Henderson and R. H. Corstorphine—The Condensation of Benzil with Dibenzyl Ketone.

Dr. W. R. Hodgkinson and L. Limpach—Some Relations between Physical Constants and Constitution in Benzenoid Amines. Part III.

Dr. George Young—The Existence of certain Semicarbazides in more than one Modification.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on Isomorphous Derivatives of Benzene.

Prof. J. Sakurai—Some Points in Chemical Education. *W. Thomson, F.R.S.E.*—On the Detection and Estimation of Arsenic in Beer and Articles of Food.

Prof. James Walker, F.R.S.—On the Nomenclature of the Ions.

Dr. E. F. Armstrong—The Equilibrium Law as applied to Salt Separation and to the Formation of Oceanic Salt Deposits.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. J. Gibson—The Electrolytic Conductivity of Halogen Acid Solutions.

P. J. Hartog—The Flame Colouration and Spectrum of the Nickel Compounds.

Dr. Farmer—The Methods of Determining the Hydrolytic Dissociation of Salts.

Dr. T. S. Patterson—The Influence of Solvents on the Rotation of Optically Active Compounds.

The Congress of the International Association for Testing Materials was held at Budapest on September 9th to 14th, under the presidency of Professor L. von Tetmajer, and was largely attended by engineers from all parts of the world. The delegates present included four from England, forty-one from Austria, three from Belgium, nine from Denmark, two from the United States, thirty-six from France, one hundred and fifty-two from Hungary, seventy from Germany, three from Norway, twelve from Italy, twenty-six from Russia, one from Roumania, three from Spain, one from Serbia, ten from Switzerland, and five from Sweden. After an Inaugural Presidential Address and address of welcome from the Hungarian authorities, a representative of each country was elected an honorary president of the Congress; Mr. Bennett H. Brough being chosen for England, and Prof. H. M. Howe for the United States. The other English and American members present were:—Sir William H. Bailey (Manchester), Mr. Bertram Blount (London), Dr. C. J. Renshaw (Ashton-on-Mersey), and Dr. R. Moldenke (New York). In

addition to the various reports of committees dealing with technical problems, the following papers dealing with Metals were read and discussed:—"On the Measurement of Internal Tension," by M. Mesnager (Paris); "On the Forms of Carbon in Iron," by Baron Jüptner (Leoben); "On Brinell's Researches," by M. A. Wahlberg (Stockholm); "On the Testing of Metals by means of Notched Bars," by M. H. Le Chatelier (Paris), by M. G. Charpy (Paris), and by Professor Belebubsky (St. Petersburg); "On Micrographical Researches on the Deformation of Metals," by M. F. Osmond (Paris); "On Metallography," by M. E. Heyn (Charlottenburg); "On the Testing of Railway Material," by M. E. Vanderheyem (Lyons); and "On the International Iron and Steel Laboratory," by Professor H. Wedding (Berlin). Several papers dealing with stone and mortars were also read, and an interesting lecture on the Iron Industry of Hungary was delivered by Professor Edvi-Illes (Budapest).

THE DURHAM COLLEGE OF SCIENCE, NEWCASTLE-UPON-TYNE.

JOHNSTON CHEMICAL SCHOLARSHIP.

This Scholarship (£60), tenable for one year, together with a PRIZE in Books to the value of £5, will be awarded on the result of an Examination in Chemistry with Crystallography or Mineralogy to be held during the week commencing SEPTEMBER 30th.

Candidates, who must be Bachelors in Science of a British University, of not more than three years' standing, are required to send in their names on or before the 27th inst. to the SECRETARY, from whom further particulars may be obtained.

UNIVERSITY COLLEGE, BRISTOL. CHEMICAL DEPARTMENT.

Professor—SYDNEY YOUNG, D.Sc., F.R.S.
Lecturer—FRANCIS E. FRANCIS, B.Sc., Ph.D.
Demonstrator—ERNEST B. LUDLAM, B.Sc.

The SESSION 1901-1902 begins on October 8th. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry and Metallurgy in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.

CALENDAR, containing full information, price 1s. (by post 1/4).
For Prospectus and further particulars apply to—
JAMES RAFTER, Secretary.

GEORGE HERIOT'S TRUST. HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. LAURIE, M.A., D.Sc.

DAY TECHNICAL COLLEGE.

Three Years' Courses of Instruction in MECHANICAL ENGINEERING, ELECTRICAL EN- GINEERING, TECHNICAL CHEMISTRY.

SESSION opens OCTOBER 1st and closes JUNE 6th, 1902.
The Classes for the Diploma in Mechanical and Electrical Engineering are recognised by the University of Edinburgh, and Students wishing to obtain a B.Sc. in Engineering, as well as the Diploma, can qualify for the Degree by taking five additional courses in the University and passing the University examinations.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with special courses in Gas and Paper manufacture, Brewing, &c., by experts, in the third year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc. in Chemistry.

Matriculation fee, 5s.; Composition fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s.

There are also Art Classes, a class in Practice of Commerce, and classes for Agricultural Students in Mensuration, Chemistry, Physiography, Drawing, Handicraft, Land Surveying, Agricultural Engineering, Book-keeping, Bacteriology.

An Extract from the Calendar of the College, giving particulars, may be had on application at the College, or from the undersigned.

BURSARIES are from time to time given by the Governors to Students attending the College, and a Travelling Scholarship of £100 has been occasionally awarded to a deserving Student.

DAVID LEWIS, Treasurer.

Heriot Trust Chambers, 20, York Place,
Edinburgh, September 6, 1901.

BATTERSEA POLYTECHNIC.

Principal and Head of Engineering Department... SIDNEY H. WELLS, Wh.Sc., A.M.Inst.C.E., A.M.Inst.M.E.
Head of the Chemistry Department... J. WILSON, M.Sc. (Victoria), F.C.S.

NEW DAY COURSES in CHEMICAL ENGINEERING, including Inorganic, Organic, and Technological Chemistry with Engineering subjects, an excellent preparation for the work of Technological and Works' Chemists. Fees, £3 per term.

DAY DEPARTMENT OF APPLIED CHEMISTRY.—Preparation for Professional and University Examinations, and for all branches of Chemical Work.

Next Session, September 16th.

For particulars see Day Classes Prospectus, price 1d., post free 2d.

BOROUGH POLYTECHNIC INSTITUTE, 103, BOROUGH ROAD (Close to the Obelisk, Blackfriars Road, S.E.).

EVENING CLASSES (LECTURES AND PRACTICAL LABORATORY WORK), commencing MONDAY, SEPTEMBER 23rd, 1901.

CHEMISTRY.—F. MOLLWO PERKIN, Ph.D., assisted by E. C. JEE, D.Sc.

INORGANIC.—Elementary: Mondays and Wednesdays, 7.30-10. Advanced: Tuesdays and Fridays, 7.30-10. Fees, 8s. to 10s. Special and Honours: Lectures—Tuesdays, 7.30-8.30; Laboratory Work—Mondays, Tuesdays, Wednesdays, and Fridays, 7.30-10. Fees, 8s. to 15s.

ORGANIC.—Elementary: Mondays and Wednesdays, 7.30-10. Advanced: Tuesdays and Fridays, 7.30-10. Fees, 8s. to 10s.

PRACTICAL ELECTRO-CHEMISTRY.—Fee, 20s.

SATURDAY MORNING CLASS, 10-1. Fee, 10s.

ELECTRICITY & MAGNETISM.—JOHN

HENDERSON, D.Sc., A.I.E.E., assisted by H. S. SAUNDERS.

ELEMENTARY (Lectures and Laboratory).—Mondays, 7.30-10.

ADVANCED (Lectures and Laboratory).—Tuesdays, 7.30-10.

HONOURS (Lectures and Laboratory).—Fridays, 7-10.

Fees, 8s. and 10s.

The fees are Sessional, September to May, 1902.

Full particulars on application.

C. T. MILLIS, Principal,
Education Department.

EAST LONDON TECHNICAL COLLEGE, PEOPLE'S PALACE, E.

Session 1901-1902, commencing September, 1901.

DAY and EVENING COURSES for the B.Sc. Degree of the University of London are conducted by the following Lecturers and recognised Teachers:—

Mathematics	J. L. S. HATTON, M.A., and W. F. S. CHURCHILL, M.A.
Physics	R. A. LEHFELDT, D.Sc., &c.
Chemistry	J. T. HEWITT, D.Sc., Ph.D.
Engineering	D. A. LOW, M.I.M.E.
Electrical Engineering	J. T. MORRIS.

The Day Courses in ENGINEERING and CHEMISTRY are also suitable for those entering manufacturing firms.

Calendar 2d. post free on application.

J. L. S. HATTON,
Director of Studies.

GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.

DEPARTMENT OF CHEMISTRY.

EVENING CLASSES, providing complete

Courses of Instruction in various branches of Pure and Applied CHEMISTRY, are held at this Institute under the direction of Mr. ARTHUR LAPWORTH, D.Sc. (London), F.I.C., &c. The Courses of Lectures and Practical Laboratory teaching are suitable for Students desiring to qualify in Chemistry at the Examinations of the London University, the Pharmaceutical Society, the Board of Education, and other public bodies. The equipment of the Chemical Laboratories has been considerably augmented and exceptional facilities are offered to advanced Students who desire to engage in Chemical Research Work during the Day or Evening. The new SESSION commences on SEPTEMBER 23rd. For further particulars apply to the Secretary.

J. S. REDMAYNE, B.A., Secretary.

THE CHEMICAL NEWS.

Vol. LXXXIV., No. 2183.

HUMUS AND THE SO-CALLED IRREDUCIBLE RESIDUE IN BACTERIAL TREATMENT OF SEWAGE.*

By SAMUEL RIDEAL, D.Sc.(Lond.), F.I.C.

ORGANIC decompositions, except those of final oxidation, are usually attended by the production of a brown colour; the colouring matter sometimes remaining in solution, and sometimes in the more energetic reactions separating in brown flakes. Types of reactions producing the colour are:—

1. Heating alone, as in the formation of caramel from sugar and its allies.
2. Heating with acids, alkalis, various salts, or even to a high temperature with water alone.
3. The change that occurs when vegetable tissues are injured or exposed to air, as seen when fruits are cut or bruised, connected with the action of the ferments called by Bertrand "oxydases."

4. Natural decay in the formation of soils, vegetable mould, and peat, and finally under certain conditions of lignite and coal.

Simultaneously with hydrolysis a smaller number of molecules seem almost invariably to undergo the opposite change of withdrawal of water, accompanied by increase in the percentage of carbon, and condensation of the molecule, producing coloured colloid compounds, which are comparatively inert, but have the power of combining with, or mordanting, large quantities of the matters in solution, both inorganic and organic. It is probable that the molecular weight of these bodies is exceedingly high. Their separation and purification is so difficult that in spite of a large amount of work it has not yet been satisfactorily accomplished, but many common properties besides colour render it convenient to group together under the aggregate term *humus* all bodies possessing such properties and produced by dehydration with limited oxidation.

Crude humus can in nearly all cases be divided into three parts:—

- I. Insoluble in alkalis, but combining with them = humin or ulmin.
- II. Soluble in alkalis, and re-precipitated by acids = humic or ulmic acids.
- III. Soluble in alcohol = resinoid bodies and so-called phlobaphenes.

Crenic and apocrenic acids are other names due to Berzelius, and more especially applied to the humous matters combined with iron in ferruginous waters and in bog deposits.

There is little doubt that the primary nucleus of all these bodies is non-nitrogenous, as it can be obtained from sugar and other substances free from nitrogen. H. Snyder (*Journ. Amer. Chem. Soc.*, 1897, xix., 738), compared the varieties of humus obtained from different organic matters kept out of contact with air for a year. He gives the accompanying figures for humus (see next col.).

C. V. John (*Zeit. Kryst. Min.*, xxiii., 289) found at the outcrop of a coal seam in Bohemia a native non-nitrogenous humic acid completely soluble in alkalis, and re-precipitated by acids of the composition C 54.98, H 4.64, O 39.98, ash 0.40.

Samples of peat examined by Tacke and Tollens (*Bied. Centr.*, 1900, xxix., 508) contained in the organic matter

Humus from—	C.	H.	N.	O.	Ratio of C. to N.
Cow manure	41.95	6.26	6.16	45.65	6.7
Green clover	54.22	3.40	8.24	34.14	6.6
Meat scraps	48.77	4.30	10.96	35.97	4.4
Wheat flour	51.02	3.82	5.02	40.14	10.1
Oat straw	54.30	2.48	3.50	40.72	21.7
Sawdust	49.28	3.33	0.32	47.07	54.0
Sugar	57.84	3.04	0.08	39.04	—

Native varieties gave the following percentages:—

					Ash.
Rich prairie soil ..	45.12	3.67	10.37	28.60	12.24
Cultivated soil ..	48.16	5.40	9.12	33.16	4.16
Never cultivated ..	44.12	6.00	8.12	35.16	6.60
Cultivated forty years	50.10	4.80	6.54	33.66	4.90

54.5 to 57 per cent of C, and 3.96 to 6.86 per cent N; an average ratio of N to C of 1 to 10. André (*Comptes Rendus*, 1899, cxviii., 513), found the ratios of C to N in the organic matter insoluble in dilute acid to be:—Peat, 9.4; cultivated soil, 6.6; moorland soil, 11.9; vegetable mould, 8.5. The form in which the nitrogen exists has been a subject of controversy. Mulder and Thénard believed it to be present in the form of ammonia, and Detmer (*Landw. Vers. Stat.*, xiv., 248), gives to humate of ammonium the formula $(\text{NH}_4)_6\text{C}_{60}\text{H}_{48}\text{O}_{27} = 6.42$ per cent N; C, 55.05; H, 5.50; O, 33.03; C/N = 8.57.

But, on the other hand, even long boiling of a nitrogenous humus with alkalis only liberates a portion of the nitrogen as ammonia. Berthelot and André (*Comptes Rendus*, cxii., 916), in their examination of the humus produced by the action of hydrochloric acid on sugar, found it to contain C, 66.41—63.91; H, 4.57—4.58; O, 29.02—31.61 ($\text{C}_6\text{H}_{14}\text{O}_{12}$ to $\text{C}_6\text{H}_{16}\text{O}_{14}$). It was insoluble in water and dilute acids. In alkalis it was partly soluble and partly insoluble; the insoluble was called *humin*, and the soluble *humic acid*. The insoluble part took up alkali (K, Na, Ba, Ca), from water, forming insoluble salts. The whole substance combined with about four molecules NH_3 , producing a gelatinous insoluble matter which, after boiling with water and magnesia, retained a proportion corresponding to the formula $\text{C}_{72}\text{H}_{33}\text{NO}_{26}$, which is that of an amido-acid formed from two molecules of the original. Adding 4 NH_3 to the first formula would give percentages of N = 7.93 and 7.57; $\text{C}_{72}\text{H}_{33}\text{NO}_{26}$ = only 1.05 per cent N. Berthelot and André considered the brown matter to be an anhydride or mixture of anhydrides, and that the nitrogenous constituents of soils (*Bull. Soc. Chim.*, 1891, v., 643), are not ammonium salts, but amides, some insoluble, which are decomposed by boiling with acids or alkalis, giving ammonia, and more slowly in the cold. The same authors (*Comptes Rendus*, 1887, 833, 911), found that a field soil contained when dry 2.35 per cent C, 0.166 N, and 0.892 K_2O , i.e., C/N = 14.1, and N in the organic matter = 3.54 per cent. The NH_3 has here been largely replaced by K_2O , which bears a ratio to the organic molecule of 19 to 100, or 16 per cent in the whole salt. To show the stability of the potash compound, only 1.6 per cent of the potash was dissolved by treatment with three successive portions of water or of 2 per cent ammonia; a somewhat larger quantity was extracted by sugar solution, by water saturated with carbonic acid, or by dilute acids. Dilute HCl removed in the cold 4.48 per cent, and even by boiling for sixteen hours only 11.4 per cent was extracted.

A sample of humus mould contained when dry 9.58 organic carbon, 0.86 N, and 1.165 K_2O , C/N = 11.1, N in organic matter = 4.5 per cent. It yielded about half its potash to dilute HCl.

Eggertz (*Bied. Centr.*, xviii., 75), investigated a large number of these brown amorphous residues, which he divides into "Mullkörper" from peat and soil, and "Humuskörper" from carbohydrates by acids. He finds that in nearly all chemical reactions they behave alike. According to him the mull substances besides C, H, N,

* Read before the British Association (Section B), Glasgow Meeting, 1901.

and O contain S, Fe, P in the organic molecule. Thirteen samples gave:—C, 40.86–56.18; H, 4.33–6.63; O, 25.09–37.98; N, 2.59–6.43; SiO₂, 0.37–10.47; P, 0.15–7.58; S, 0.55–2.09; Al₂O₃, Fe₂O₃, 0.38–3.90. "The silica is probably present as NH₄ silicate. Both mull and humus substances contain ash constituents which can scarcely be considered as mere inorganic impurities" as they cannot be washed out (?) "Besides the N present as ammonium-mull salts, they contain N which is not removed by repeated solution and re-precipitation. Eight samples containing 5.8 to 10.7 N, at the end retained 2.12 to 5.30 per cent. A great part is diffusible, hence would be taken up by plants. "The constituents derived from the oxidation of mull substances are more important as a natural source of plant nutrition than the mineral phosphates and silicates."

L'Hôte (*Journ. d'Agricult. Pratique*, 1890, 365) found in humic acid from garden soil 4.73 per cent N; from arable soils 6.07 and 5.41 per cent. Thénard obtained slightly higher figures with humic acid from rotted farm-yard manure. Sestini boiled crude humic acid with 2 per cent soda for thirteen and a half hours, and little more than half the nitrogen was expelled as ammonia, while only a relatively small amount of ammonia was formed by boiling with 10 per cent hydrochloric acid for twenty-four hours. By the action of nitrous acid he obtained evidence of the presence of amides, but a considerable portion must have been present in an organic state (*L'Orosi*, 1898, xxi., 1–6). He obtained furfuraldehyde by the action of hydrochloric acid on crude humus from soil, purified humic acid, and the humous substances obtained from sugar, showing another common property of the humous group.

In view of the extraordinary tenacity with which humous bodies retain inorganic constituents, there is no improbability in nearly the whole of the nitrogen being present in the ammonio- or at least amido-form. As showing this avidity of combination, Rodzanko (*Journ. Russ. Chem. Soc.*, xxii., 208), found that humin absorbs various inorganic substances from aqueous solution, as sulphates, chlorides, phosphates, and carbonates, salts of aluminium, and alkaline silicates, and that humic acid dissolves and decomposes several otherwise insoluble inorganic compounds, and decomposes silicates. "Humin compounds already containing a given element absorb substances containing this element more readily than other substances; it seems that metallic derivatives of humic acid are stronger acids than the original acid," depending on the poly-basidity and the formation of unsaturated acid salts. Bréal proved that an alkaline humate solution was directly absorbed by the roots of plants (*Ann. Agron.*, 1894, xx., 353).

A further light was thrown on the functions of humus, especially in connection with its occurrence in water and in sewages, by the researches of Adeney ("Dissolved Gases and Fermentative Changes," *Trans. Roy. Dub. Soc.*, September, 1895). A deep brown extract from peat by water and a little soda was allowed to ferment in air six months, then mixed with five volumes tap-water, and allowed to settle. It was known that peaty matters in river waters, having arrived at a stable condition in flow, suffered little oxidation or change. But, on the other hand, these substances, when fresh, undergo in water a considerable alteration, since the unoxidised peaty matter in upland surface water showed a ratio of carbon to nitrogen of 11.9 to 1, whereas after exposure to oxidation in lakes or large reservoirs the proportion was 5.9 to 1. These proportions of C to N are very similar to those found in the fermented matters resulting from the complete fermentation of sewage during slow sand filtration, *i.e.*, 9.6 : 1 to 6.3 : 1.

The fermented organic matter formed during slow filtration of sewage, besides showing similarly high proportions of C to N as peaty matter and similar resistance to fermentation, also resembles peat in colour and optical properties. Thus, when derived from a sewage filtrate of

brown tint, the ratio of C : N was 7.1 : 1; it was not distinguishable from peat by the spectroscopic (Hartley), giving identical ultra-violet absorption. Adeney early noticed that in every experiment in which oxidation of ammonia to nitric acid had been complete, small quantities of peaty or fermented organic matters were always present, that they were necessary for the nitric fermentation of ammonia, and that if absent, abundant nitrite, but no nitrate, was formed.

Experiments showed that in presence of large quantities of water and organisms, the peaty matter fermented to carbonic acid and nitric acid. If not diluted NH₃ is absorbed. In some experiments the oxygen of the peat itself must have taken part. *The peaty matter absorbs considerable quantities of ammonia.* An important conclusion of the research was that in the absence of peaty matters we get nitrous fermentation of ammonia, in their presence we get nitric fermentation of either ammonia or nitrous acid. "The presence of peaty or humous matters appears to preserve the vitality of nitric organisms during the fermentation of ammonia, and establishes conditions whereby it is possible for the nitric organisms to thrive simultaneously in the same solution with the nitrous organisms."

In a further research (*Trans. Roy. Dub. Soc.*, August, 1897), he established the similarity to peat and soil humus of the humus from fermented sewage. The latter was slowly but completely soluble in sodium carbonate, to a deep brown solution indistinguishable from that from peat or garden soil, the ratio of C to N being 6.84 : 1. Culture solutions of this were allowed to ferment in closed vessels; the action was slow, but the phenomena were:—CO₂ was produced, dissolved oxygen disappeared, there was no change in the free nitrogen, ammonia was converted into nitrate, and no nitrite was formed. Humus from peat behaved in exactly the same way. He concludes that "organic matters which are themselves the result of bacterial fermentative changes, or a carbon oxidation of fresh organic substances, take an active part in any subsequent fermentation of ammonium compounds with which they may be mixed, and determine the nitric fermentation of these compounds. . . The organic products of the first stage, or fermented organic matters, never give rise to the formation of ammonia," and therefore are generally non-offensive.

I have examined a number of these humous residues from the bacterial treatment of sewage. At the end of 1898 I found the peaty deposit in the Exeter septic tank to contain:—

	No. 1.	No. 2.	No. 3.
Distance from bottom, inches	3.	9.	15.
Organic matter, per cent.	32.35	32.40	31.31
Ash, per cent	67.65	67.60	68.69
Nitrogen, per cent	2.38	2.34	2.45
Percentage of N in organic matter	7.36	7.22	7.82
Ratio of carbon to one of nitrogen	6.8	6.9	6.4

Microscopical Characters.

1. Black amorphous matter; small sand particles; fragments of muscular fibre, dark coloured and corroded, and of other animal tissues; large amœba, cladotrich, micrococci, and bacilli; fragments of faecal matter, vegetable tissue, and hairs.

2. Spiral vessels of a plant, anguillulæ, egg of an entozoom; fewer amœba, otherwise like the last.

3. Anguillulæ, vegetable hairs, and spiral vessels; faecal fragments rather abundant; sponge spicules; animal hairs; no amœba and very few muscle fibres; otherwise like the preceding. It will be seen that the older matter is mixed with recent substances lately arrived in the tank.

I have also analysed the black deposit from the first contact bed at Hampton (June, 1900); it contained:—

Water	7.18
Ash	48.37
Organic matter	44.45

Total nitrogen	4.788
Percentage of N in organic matter	10.79
Organic nitrogen	3.058
Percentage of organic N in organic matter.	7.12
Combined ammonia	1.73
Ratio of carbon to one of nitrogen	7.0

The ash contained:—

Oxide of iron and mineral salts	17.00
Coke	4.18
Siliceous matter	27.19

48.37

The organic matter was therefore closely related to humus, and was similar to that found in the septic tank. A microscopical examination showed large numbers of anguillulæ, with amœbæ, a few rotifers and flagellate infusoria; aquatic larva cases and portions of insects; a few animal hairs (possibly human), and some isolated fragments of muscular fibre; diatoms and desmids (*Synedra*, &c.); vegetable débris; fragments of wood, epidermis, and leaf hairs; ducts of ferns, spiral vessels, straw and grass stems; a large quantity of dark brown amorphous matter of humous character; crimson particles and dyed fibres, blue and orange; fragments of coal and coke; sand; and carbonate of lime crystals.

Still more recently I collected some of the black floating particles from Stoddart's continuous filter at Knowle, Bristol (on September 28th, 1900). The total weight of deposit was 4.37 parts per 100,000 of effluent; it contained:—

Mineral matter	31.91
Organic matter	68.09

100.00

Organic N	4.69
Combined ammonia	0.57
Percentage of organic N in organic matter ..	6.88
Ratio of C to one of N	7.3

The microscopic examination showed:—Aquatic larva cases, fragments of winged insects, numerous anguillulæ, crustacea (*Daphnia*), rotifers, infusoria (monas, paramœcium, vorticella), algæ (cladophora and species of conferva), cladothrix, beggiatoa, fungus mycelium, black particles (probably coke), brown amorphous matter, siliceous particles, vegetable hairs and fibre (*Trans. Soc. Engineers*, 1900, p. 247).

The finer portion of the organic matter collected from crude sewage by screening contains only 2 per cent of nitrogen. This low figure is of course due to the considerable quantity of undecomposed cellulosic matter present.

In 1901 I found in a number of dark muds from an estuary:—

Organic matter.	% N in organic.	Ratio C/N.
19.46	4.00	12.5
11.54	3.15	16.0
13.91	3.69	13.5
18.14	5.68	8.8
17.65	4.39	11.4
19.14	4.38	11.4
22.24	4.15	12.0
10.23	4.52	11.0
14.31	3.36	15.0
17.35	3.23	15.5
16.55	2.44	22.3
17.18	2.80	17.8

In conclusion, if sewage has undergone proper bacterial fermentation, the small quantity of peaty deposit, called by Cameron "burnt-out ash," and by others "irreducible residue," is of the nature of humus, and practically inoffensive. Kenwood and Butler state that at Finchley in

1900 the deposit from open septic tanks could be removed with little offence, and has been spread, without nuisance, over small areas of land in the neighbourhood. It has also the agricultural value of humus. Like peaty matters generally, it has a function in encouraging, when in small quantity, the nitrifying actions in the final oxidation, and itself undergoes slow oxidation to carbonic acid and nitrate.

SOME POINTS IN CHEMICAL EDUCATION.*

By JOJI SAKURAI, LL.D.,
Professor of Chemistry in the Imperial University of Tokyo, Japan.

CONSIDERED from a certain important point of view which, so far as I know, has not hitherto been explicitly stated, chemical education, as at present generally carried on, appears to me to be inefficient and unsatisfactory, and no better opportunity has presented itself, than on the present occasion, of submitting the matter to your consideration. It is for this reason that I wish to address you.

You are all aware that chemistry has made a marvellous and wonderfully rapid progress within the last fifteen years. Now, it is not my intention to dwell upon the ground on which the structure of modern chemistry, if I may so call it, stands, nor is it, indeed, necessary for me to do so, since its soundness is no longer disputed; it is rather to the fact that, in spite of the high educational value which it possesses, its teaching is unduly neglected, that I wish to draw your attention.

The recent progress in chemistry is characterised by the fact that not only experimental means of investigation have been extended, enriched, and made accurate, but also a number of comprehensive and fertile ideas have been developed one after another, and deductive methods of enquiry made possible, and found to be exceptionally fruitful; chemistry has, in fact, thrown off much of its empirical character, and established itself to be a truly rational science. The educational value which it has thus acquired is enormous, a student of modern chemistry having ample opportunities of cultivating the power of observation, and the faculty of reasoning at the same time. Neither an essentially descriptive science, such as mineralogy, botany, or zoology, on the one hand, nor an essentially abstract science, such as mathematics or logic, on the other, possesses in itself this two-sided advantage. Physics is the only science which, for years, has enjoyed that privilege, but now chemistry has come forward, combining, as it does, experimental and deductive methods of study in due proportion; and its educational value must be regarded as even greater than that of the sister science, for the field of investigation, which a student of modern chemistry has at his command, is more extended and more fertile than that presented to a student of physics. It is more extended because many of the processes going on around us are of the chemical nature, and it is more fertile, because much of it has been left uncultivated or only imperfectly cultivated from want of the requisite means now supplied.

Not only is modern chemistry a keen weapon of sound and scientific education for those who would become pure chemists, but also for those who would have to apply the knowledge of that science in special directions, such as physiology and chemical technology, inasmuch as its conceptions are exceedingly comprehensive and fruitful, and have not only found their applications in these directions, but have also already led to some important practical results.

For boys in secondary schools, teaching of chemistry from the point of view recently attained is no less important, as it puts the most important facts of the science in a clear, intelligent, and rational form, supplying requisite food for the healthy development of their brain.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

Notwithstanding these evident and exceptional advantages which the teaching of modern chemistry affords, it is still taught, to a great extent, in the same dry and merely descriptive way as in old days, explanations which are in direct opposition to well established facts being, moreover, not unfrequently given. Neither repetition of names, formulæ, preparations, properties, and so forth, and description of other isolated facts, nor even exercise in qualitative and quantitative analysis, can be regarded as a source of much mental satisfaction to the student, capable of vigorous, or even moderate, exercise of the mind; and little or no opportunity being given of satisfying his mental aptitude, he may think chemistry a very uninteresting subject, and turn away from it. It is, I think, both possible and probable that we are in this way discouraging some of the brightest students from coming to us, or losing them from among us. At any rate it appears to me to be plain that we are not making use of the very keen educational implement which we possess to its best advantage, and for the interest of our science and profession this state of things should be speedily remedied.

Granting, then, that the present system of teaching chemistry is inefficient and unsatisfactory, and that a more free and general introduction of modern views and methods into it is necessary, I would venture to make a few suggestions for the remedy.

One of the remedies would, I think, be to remove certain misconceptions which seem to prevail pretty freely. Now, the means by which the recent marvellous development has been achieved—a development almost unparalleled in its magnitude and importance in the history of chemistry—is essentially what is called “physical,” and, as a consequence of this, what I consider to be a misleading and unfortunate name, that of physical chemistry, has come into general use. It is misleading, because to those who have not watched the progress with special interest, the analogy, in name of physical chemistry with physiological chemistry or agricultural chemistry may suggest an idea that it is only a special branch of chemistry. To such an audience as I have now the honour of addressing it is scarcely necessary for me to say that such an idea is entirely mistaken. Whilst physiological or agricultural chemistry applies chemical methods to questions essentially physiological or agricultural, the so-called physical chemistry pervades the whole domain of our science, and treats of chemical problems which are specially fundamental and important, only the methods of research and the instruments employed are mostly those hitherto exclusively used by physicists. These methods and instruments are, however, no longer merely physical, but are also chemical; the determination of electrolytic resistance, for example, is now as much a chemical operation as weighing or measuring, and a galvanometer as much a chemical apparatus as a balance or a litre flask. The name of physical chemistry is not only misleading but also unfortunate, because on account largely of the above misconception, as I take it, not only its cultivation but also its teaching has been much neglected. I would therefore suggest that the name *General Chemistry* should exclusively be used in its stead. Many of you would, no doubt, think this a very trifling matter, and ask, “What’s in a name?” but I think there is a great deal in a name, especially as in this case, when it is misleading and liable to hinder progress. Ostwald was perfectly right when he gave the title “Allgemeine Chemie” to his *Lehrbuch*, but I think he made a regrettable mistake in calling that important periodical, edited by himself and van’t Hoff, *Zeitschrift für Physikalische Chemie*.

Another misconception, which seems to have crept into the minds of many, and which has also apparently prevented a more rapid diffusion of modern ideas, relates to the use of mathematics. It is very often stated that as the treatment of general chemistry requires higher mathematics, it is neither possible nor desirable to introduce it into elementary teaching, but it appears to me

that in this opinion there is a confusion of ideas. It is true that for a detailed study and cultivation of general chemistry, a fair knowledge of higher mathematics is both desirable and necessary, and I think it well that this fact should be clearly and generally recognised, and that students of chemistry should be encouraged to acquire this knowledge, preferably from a physicist or a chemist rather than from a pure mathematician. But the teachings of general chemistry can be introduced into elementary text-books without any mathematics, save perhaps a few of the simplest algebraic formulæ, and yet in a concise, useful, and interesting form; moreover, simple and appropriate lecture experiments, illustrating the laws of chemical dynamics or the theory of solutions, can be easily contrived. As a means of diffusing the knowledge of, and increasing the interest in, general chemistry, I would therefore suggest that, for the sake of school teachers, courses of lectures in which general chemistry is amalgamated with descriptive matter should be given, say during the summer vacations, and that also writing of elementary text-books on the same plan should be encouraged.

There is another point which I wish to mention. The attempt to give a fair training in general chemistry over and beyond what the student has been accustomed to learn would no doubt take up too much of his, as well as of the teacher’s time, but I believe that some portions, and even a great deal of the descriptive matter usually given in lectures can be cut off, not with inconvenience but rather with advantage, because in the class-room the attention of students should be more directed to points of general importance and interest, leaving details to be read up by them, and that the time usually devoted to analytical work in the laboratory may also be conveniently shortened, because what the student should learn from it is rather principles and methods of analysis than mere practical skill. Chemical laboratories of universities, and even of colleges, should be institutions which contribute to the sum total of our knowledge, and in which men are trained with that object in view, and not mere workshops for apprentices.

Before concluding, I wish to draw your attention to yet another point, a point which lies on a somewhat different line of thought, but still connected with the question of chemical education. You are, no doubt, aware that an International Committee on Atomic Weights was organised a year or two ago, on the invitation of the German Chemical Society, and with the view of settling upon atomic weights for ordinary use, and that as the standard atomic weight $O = 16.00$ was adopted by a very large majority. There are, as is well known, many and strong reasons for adopting this standard; yet it appears that outside the International Committee there were several chemists who preferred the standard $H = 1.00$, and on whose account the German Committee was led to publish two tables of atomic weights, one on the oxygen standard and called “International Atomic Weights,” and the other on the hydrogen standard, and called “Dydactic Atomic Weights.” Pedagogic reasons seem to be the chief ground of their giving preference to the hydrogen standard, but I must confess that I am unable to see why. If in teaching chemistry atomic weight is treated before molecular weight, if the student is to be told that the molecular weight of a substance is obtained by summing up the atomic weights of the constituent elements, and if he is made to believe that an atom of such and such an element is so many times heavier than that of hydrogen; if, in short, the most important stoichiometrical laws of chemistry are to be put in the background, then I can understand that there is a preference to the hydrogen standard, but it appears to me that such a method of teaching is a gross mistake, taking the student a century back, and putting him in the same difficulty as Dalton was placed, a difficulty which took fifty years of progress to remove. Now, what are atomic weights, and how are they determined? If, for example, we wish to determine

the atomic weight of carbon, have we not, first of all, to ascertain the molecular weights of as many of its compounds as available? Have we not then to determine the quantities of carbon contained in one molecular weight of each of these compounds? And do we not finally regard the greatest common factor among the numbers, representing these quantities of carbon, as its atomic weight? The very nature of the constants which we call atomic weights requires them to be determined after molecular weights, and it is essential, therefore, that we should first agree upon some one molecular weight as the standard of comparison. Now, in fixing this standard of molecular weight I do not see any better pedagogic reasons for adopting hydrogen and calling its molecular weight 2, than adopting oxygen and calling its molecular weight 32, nor do I see any advantage in defining the common unit of atomic and molecular weights as $\frac{1}{2}$ of the molecular weight of hydrogen, over defining it as $\frac{1}{32}$ of the molecular weight of oxygen. The question simply lies between the two numbers, 2 and 32, both of which are arbitrary, and either of which serves to express with equal clearness the stoichiometrical relations of hydrogen or oxygen to other substances. Looked at and taught from this point of view, as, I think they should be, the quantitative laws of chemical combination do not give preference to the hydrogen standard for their elucidation and illustration; on the contrary, its formal adoption is liable to increase the tendency, already too great, of giving to students erroneous notions on atomic and molecular weights, and of making them think that hypotheses are statements of facts. At the same time, atomic-molecular hypothesis has nothing to lose from the adoption of the oxygen standard. It appears to me therefore that pedagogic reasons go against the adoption of the hydrogen standard, rather than for it.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 145).

In order to obtain more exact conclusions with regard to the stability of gun-cotton we next investigated the effect of treating successively with cold, running, and hot water.

In the first experiment the gun-cotton was treated for three days with cold water. It was placed in a large porcelain dish, which was supplied hourly with fresh water, the nitration product being at the same time well pressed on the vacuum pump. After this followed a similar treatment for two days with hot water (90–93°). One-half was then dried in a dry current of air at 40°, the other in the vacuum desiccator over sulphuric acid. The latter reacted with the "Abel test" at 70° after 4' 15", the former after 2' 1". The stability was therefore quite insufficient. According to Thomas, the Abel test when compared with his own sometimes gives directly contradictory results; accordingly we wished to see how this product would behave towards Thomas's test. Two samples each of 1.2 grm. were placed in an oil-bath furnished with a temperature regulator, and slowly warmed up. After about half-an-hour a violent explosion occurred, which shattered the apparatus. The temperature cannot have been above 100°, for 92° was noted just before the explosion occurred. In this case, therefore, the agreement with the result of the Abel test was only too apparent. Hence, for products of which great stability is not to be expected, the test proposed by Thomas is not to be recommended, having regard to the safety of the experimenter.

In a second experiment, the product was treated, in the way described above, for one day with cold water, three days with hot water, and finally three days more with

running water; but here also a sufficiently stable product was not obtained. The Abel test gave 4–6 minutes.

A continuous rotation of the gun-cotton during the washing in running water did not serve materially to improve the results.

The nitration product was now, in a further experiment, washed in a manner similar to experiment 2. After this, seven days' treatment with cold, hot, and running water, there can only remain small traces of residual acids. If the stability were really alone dependent on the removal of these last traces of acid, it would be possible to increase it considerably by neutralisation of the same. The alleged cause of the difficulty of removing the final traces of acid is that the nitration mixture penetrates the innermost cells and particles of the cotton; but if we now finally treat with dilute alkali there is no obvious reason why the latter should not penetrate into the cells with equal facility. Hence, after the above-mentioned seven days' treatment, the product was treated one day longer with hot water, with the addition of 0.2 c.c. N/10 soda solution. The water was still alkaline at the end; it may therefore be safely concluded that there was no longer any acid present; yet the Abel test gave eight minutes only, which still showed insufficient stability. Thus, for improvement beyond these limits, it was necessary to take a fresh starting-point, dependent on other causes. The opinion has already been given that one of these causes may be the presence of foreign matters in the gun-cotton. These might arise from the action of the nitration mixtures on the impurities contained in the cellulose, or they might be ascribed to secondary actions of the acid mixtures on the cellulose itself. Lenk and Cross have recently published a research on this point. They succeeded, by treating with acetone so dilute that it had no solvent action on the gun-cotton itself, in extracting a small quantity of foreign matter, and by this means the stability was considerably increased. This body, which lowers the stability, has not yet been further examined; it contains 9–12 per cent nitrogen. In this way better results should be obtained than by prolonged boiling. It may here be mentioned that, simply by means of boiling for three days, we obtained a stability of more than fifty minutes. The maximum from Cross's experiment was fifty-five minutes. It is an established fact that by boiling for a relatively short time the stability is considerably more increased than by lengthened treatment with cold and hot water.

In all succeeding experiments we proceeded as follows:—After removing most of the adherent nitration acid with cold water the gun-cotton was cut up as finely as possible with scissors, and then boiled with frequent changes of water. In this manner a fairly high stability is obtained in three to four days. It is, as already remarked, unlikely that this result is entirely dependent on the removal of all traces of acid. "Chemically pure bandage wadding" was always used, so it is only conceivable that there may be a secondary action of the nitration mixtures on the cellulose itself.

The stability cannot upon these lines be increased beyond a certain limit. An absolutely stable body is not obtainable, for gun-cotton is in itself an unstable product.

Spica has shown that even the most carefully purified gun-cotton decomposes to a slight extent.

A distinction might therefore be made between a temporary instability caused on the one hand by traces of residual nitration acids, and on the other hand by the presence of foreign matter, and a permanent instability due to the nature of the nitrocellulose molecules.

(To be continued).

Society of Arts Examinations, 1902.—The Programme for 1902 is now ready, and may be had (price 3d., post free) on application to the Secretary, Adelphi, London, W.C. The Examinations will commence on Monday, April 14th, and will be concluded on Thursday, April 17th.

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

SOME REMARKS ON THE PLACE OF
HYDROGEN IN THE PERIODIC SYSTEM.

By GEOFFREY MARTIN.

HYDROGEN for many years has been associated with the alkali metals in the periodic arrangement of the elements. The fact which weighed most in attributing such a position to this remarkable element was the undoubted metallic properties it displays when it enters into the composition of acids and salts. In such bodies we find metals and hydrogen are capable of mutually replacing each other; the acids, in fact, may be regarded as hydrogen salts.

The analogies between hydrogen and the metals are too well known to be discussed here.

Of recent years, however, many eminent chemists have expressed doubt as to the advisability of placing it at the head of the alkali metal group.

Some have even suggested a position at the head of the chlorine group of elements (Crookes, *Proc. Roy. Soc.* 1898, 408; Masson, *CHEM. NEWS*, 1896, lxiii., 283).

The cause which has undoubtedly led to such a revulsion of feeling may be traced to Graham's unfortunate interpretation of the remarkable power which Pd has of occluding it. He believed a Pd-H alloy was formed. It has since been proved that in general hydrides of the various metals have anything but metallic characteristics. LiH and CuH, for example, are respectively white saline and brown powders, quite different in character to alloys.

Graham believed H to be a light volatile metal, while Dewar has proved it to be a colourless liquid resembling strongly a liquid hydrocarbon like CH₄. Liquid hydrogen, in fact, is devoid of metallic properties of any description.

Two main objections have been raised against the position given to H as the first element of the alkali metal group, viz. :—

- (1). Hydrogen itself has no metallic characters; therefore it cannot belong to Group I.
- (2). The atomic weight of hydrogen is incompatible with such a place; for (a) the difference between the atomic weights of H and Li is only 6, while the difference between the elements of series 2 and 3 of Mendeleeff's table averages 15 to 20. (b) The position of hydrogen at the head of the alkali metals will necessitate six gaps for undiscovered elements between H = 1 and He = 4.

The following periodic table shows this :—

PERIODIC TABLE.

Series.								
I.	H 1	*	*	*	*	*	*	He 4
2.	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	Ne 20
3.	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5	Ar 40
4.	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 54	

halogens), while metals generally, including the alkali metals, are non-atomic, both in the gaseous and dissolved condition.

All such objections arise out of, and vanish with, the assumption that if H belongs to Group I. it must have metallic properties—an unnecessary and unjustifiable assumption; for while most of the groups of the periodic table begin with non-metallic elements, the heavier elements of the same groups are undoubted metals; increase of atomic weight invariably brings out metallic properties.

For example, carbon and nitrogen are without doubt non-metals; nevertheless, tin and lead of the one group, and antimony and bismuth of the other, are metals. In considering the relation hydrogen bears to the alkali metals it must be remembered that Li has an atomic weight seven times that of hydrogen. It is not, therefore, surprising that while H has no metallic properties Li should be a pronounced metal. In Group III., for example, boron is a pronounced non-metal; nevertheless, the next group element to it—aluminium—with an atomic weight less than three times that of boron, is a most decided metal. Again, in Group IV., titanium with an atomic weight only four times that of the emphatic non-metal carbon exhibits metallic characteristics. Many other examples could be given. The fact that hydrogen itself is devoid of metallic characteristics has, therefore, little weight as an argument for rejecting it from Group I. Its atomic weight is much too low for it to individually exhibit a metallic character in its *physical characteristics*.

On the other hand, in its chemical properties it fore-shadows strongly the coming metallic properties of the succeeding heavier elements of the group.

Indeed, as a rule, the chemical characteristics of an element are far surer indications of its analogy to other elements of the same group than are its individual physical properties. Thus, while the gaseous nitrogen is as unlike as can be physically to As or Sb, nevertheless such elements produce compounds which resemble each other to a truly startling degree. Indeed, one could hardly believe that such dissimilar bodies as N, P, As, and Sb could produce such similar compounds as N.Et₄OH, P.Et₄OH, As.Et₄OH, and SbEt₄OH.

With decreasing atomic weight a chemical similarity or behaviour lingers among elements of any one group long after all physical resemblance has disappeared.

The fact that hydrogen still plays its part as a metal in acids and electrolytes generally may be taken as an illustration of this property in the alkali metal group.

(1). The first objection includes all those arguments based upon the absence of metallic characteristics, such as the fact that hydrogen does not form alloys, or the fact that the H molecule is composed of two atoms (like the

(2). We will now proceed to deal with the second objection. (a) It is true that the difference between the atomic weights of Li and H is 6, while the differences between the elements Na and K, Be and Mg, B and Al,

&c., average 15–20. But this is, so to speak, a mere local effect depending on the fact that we are subtracting atomic weights. If we divide them instead we will actually get evidence in favour of the position of H at the head of the alkali metals.

Thus we have:—

$$\frac{K}{Na} = \frac{39.1}{23} = 1.7,$$

$$\frac{Na}{Li} = \frac{23}{7} = 3.3,$$

i.e., the ratios are in the one case nearly double that in the other. If we imagine a similar relation holds for the next ratio between Li and the element above it we have:—

$$\frac{Li}{H} = 3.3 \times 2 = 6.6.$$

The actual ratio, $\frac{Li}{H} = 7$, is close to this.

It is thus seen that a different way of manipulating the atomic weights leads to quite different results.

We have *a priori* as much right to use the one method as we have to use the other, and the conclusions deducible from the one method have an importance equal to those deducible from the other.

Thus, the objection to the position of H in Group I. on account of the value of its atomic weight falls completely to the ground.

(b) The position of H at the head of the alkali metals will necessitate six gaps for undiscovered elements. This has been urged as an objection (Masson, *loc. cit.*).

We have not the slightest reason for doubting the existence of such elements. The mere fact they have not been yet isolated counts for little. With the new horizon that has opened out with the discovery within the last few years of some nine or ten new elements—some such as argon occurring in quite appreciable quantity—indicates the probability that with more refined and at present unknown methods of research will lead to the discovery of many other elements. For example, the Curies, by working with the electrometer as a chemist works with a balance, have discovered several heavy radio-active elements.

We may therefore conclude that, not only does hydrogen find its true place at the head of the alkali metals, but also that the arguments urged against such a position when examined are found to be devoid of weight.

Professor Orme Masson (CHEM. NEWS, lxxiii., 283), has put forward the following arguments for attributing to hydrogen a position as the first member of the halogen group of elements. The matter is of some importance, for two famous English chemists seem to have given their adherence to this view (Crookes, *Proc. Roy. Soc.*, 1898, 405; Ramsay, *Proc. Roy. Soc.*, January 8th, 1901). We will deal with Masson's arguments in detail:—

1. *The atomicity of hydrogen (H₂) is the same as that of the halogens; so far as evidence goes the alkali metals are, on the contrary, monatomic in the gaseous and dissolved conditions.* This difficulty vanishes if we give up the view that hydrogen is a metal. Even at its best the argument is of doubtful weight in adjudicating a position in the periodic table; for instance, while the N molecule is N₂ the P molecule is P₄, yet both elements undoubtedly belong to the same group.

2. *The gaseous character of hydrogen agrees with a position at the head of the halogen group.* On the other hand, it can be argued that the exceeding lightness of the H molecule is a powerful factor in causing it to be gaseous.

It must be remembered that if H be given a position at the head of the alkali group, Li is seven times as heavy as it. P, which is only a little more than twice as heavy as N, is a solid at ordinary temperatures, while nitrogen is one of the so-called "permanent" gases. The same is true for oxygen and sulphur. It is therefore scarcely surprising that Li with an atom seven times as heavy as that of H should be a solid, while H is a very volatile gas.

3. *The evidence which can be drawn from the atom weight of hydrogen favours a position in the chlorine group.* We have discussed this point, and have shown the facts can be interpreted as an argument for a position in Group I.

4. *In hydrocarbons and other organic compounds hydrogen and the halogens can mutually replace each other, often with no more effect on the general properties of a compound than is produced by the substitution of one halogen for another.* This is to some extent true, but is merely an example of a principle which has been known for many years. According to Laurent and Gerhardt the characteristic properties of a compound depend more upon the way in which the constituent atoms are arranged in the molecule than upon the chemical nature of the atoms themselves, so much so that even if the most diverse radicals entered into a compound by displacing another radicle they would, in virtue of their position in the molecule, continue to perform the function of the displaced radicle, and thus would not materially alter the fundamental characteristics of the body into which they entered.

It is thus seen that little can be said in favour of placing hydrogen at the head of the halogen group of elements. On the other hand, the following arguments are in direct opposition to such a view:—

(1). If we consider the capability of the elements I, Br, Cl, and F to combine with oxygen, we find that, while the oxides of iodine are, comparatively speaking, stable, the oxides of Br and Cl are much more unstable, and decompose explosively on the slightest provocation, while the oxide of F appears to be too unstable to exist. It is clear, therefore, that as the atomic weight decreases from iodine downwards in the halogen group, the capacity for combining with oxygen decreases, until finally F refuses altogether to form an oxide. If hydrogen was really a member of this group, with an atomic weight lower than F, we should expect it to absolutely refuse to combine at all with oxygen.

As a matter of fact H does unite with oxygen with great energy to form water—a most stable substance totally unlike the unstable oxides of the halides.

(2). The halogens combine energetically with Na at ordinary temperatures, with the evolution of great heat. H, however, shows but little affinity for the alkali metals, and usually requires to be heated before a noticeable amount of combination occurs. Further, such hydrides are most unstable bodies (e.g., Cu₂H₂)—for instance, when NaH is treated with Hg, the Na and the Hg unite, and hydrogen is expelled—a behaviour totally different from the stable halides of the alkali metals.

It is needless to give any other examples. They can be multiplied indefinitely.

Indeed, the entire chemical behaviour of hydrogen and its compounds most decisively shows it has utterly nothing in common with the halogens.

On the other hand, the compounds of H call to mind the compounds of the alkali metals.

Its chloride is a stable body formed with evolution of heat and light; its oxides resemble those of the alkalis; H₂O resembles KHO, and acts as a feeble base. For example, both H₂O and KHO are capable of causing hydrolysis, while H₂O₂ is analogous to the peroxides of sodium and potassium. Hydrogen also forms sulphates, nitrates, oxalates, &c., all analogous to similar compounds of the metals.

There is thus a very real analogy between the compounds of H and those of the alkali metals.

Bristol, September 1, 1901.

Generator Gases produced by means of "Linde" Air.—The Verein zur Beförderung des Gewerbefleisses in Berlin has offered a prize of £150 (3000 marks) and the large gold medal for the best work on the results of experiments with generator gases, produced by concentrated oxygen ("Linde" air). The work must be given in by November next.

ELECTROLYSIS IN BLEACHING TEXTILES.

THE application of electricity to manufacturing processes has long occupied the attention of scientific men and inventors. Every effort has been made in recent years to simplify and cheapen the cost, not only of the necessary machinery, but of chemical elements as well. Some Germans have invented an apparatus for producing "chemic," or bleaching liquor, out of ordinary brine, the product being sodium hypochlorite, which is attracting considerable attention among textile manufacturers on the Continent. It is claimed that the chemic obtained by this method produces a whiteness superior to that of the ordinary English bleaching liquor.

The following detailed description of the invention and its improvements may be of interest to the textile manufacturers of the United Kingdom:—

The ordinary apparatus is extremely simple, being mainly a trough or box of slate, swung on trunnions, in a suitable frame, with an inlet for the brine, and an outlet for the sodium hypochlorite resulting from the passage of a current of electricity through the brine as it runs through the box, the poles or electrodes being placed at opposite ends of the box.

Thermometers are suspended at the inlet and at the outlet in order to show at a glance the strength of the sodium hypochlorite, it having been found that every rise of 5° C. corresponds to 1 grm. of free or active chlorine per litre (equal to 62 grains per gallon).

In order to clean the apparatus the thermometers are removed, and the trough reversed and cleansed with a hose-pipe. The electrodes last about one year, and can be easily replaced. The bleaching liquor, the product of the apparatus, is suitable for bleaching raw cotton, yarn, cloth, lace, and embroidered fabrics made of cotton, linen, jute or flax, pulp, paper, &c. It advantageously replaces chloride of lime for these purposes.

The advantages claimed for this system are:—

1. The electrolysed solution possesses high decolorising or bleaching power.
2. The goods treated in the ordinary process of bleaching are not harmed, and there is scarcely any appreciable loss in weight.
3. Lime or magnesia salts are not deposited on the cloth, thereby eliminating trouble in subsequent dyeing and printing.
4. Constant strength of liquor, which can be used as fast as made, if desired.
5. Economy in cost of production.

The apparatus is constructed in three sizes, to produce per ten hours respectively, 350, 650, and 1000 gallons of electrolysed solution, containing 3 grms. per litre (equal to 186 grains per gallon), of active chlorine, prepared from brine of a strength of 6° Baumé.

For purposes of comparison we may say that 650 gallons of the electrolysed solution contain 20 pounds of active chlorine; to obtain from chloride of lime 20 pounds of active chlorine it would be necessary to use 70 pounds of bleaching-powder, and the resulting 650 gallons would be found to give inferior results. The reason of this difference lies in the constitution of the electrolysed liquor, which has been found to contain the following:—Free chlorine, free hypochlorous acid, sodium hypochlorite, and sodium chlorate. It is chiefly the free hypochlorous acid which causes the rapid bleach. This solution is harmless to the fibres of the threads—the best proof that they are not injured being that goods bleached by electrolysis only lose about 2 per cent, as against some 8 per cent for chloride of lime bleach.

When making further comparisons between the new and the old methods, it is well to bear in mind the fact that chloride of lime quickly loses its strength. It is invariably assumed to be of some given standard, but as the hydrometer test is deceptive and other tests are troublesome, guessing is generally resorted to, and cloth is often spoiled. In this apparatus the difference between the

readings of the two thermometers is a ready and infallible test, though that is scarcely needed after once regulating the flow of the brine and the electrical current. The electrolysed liquor is always of one strength; mixing or reducing is not necessary, neither does the apparatus need attention. Rock-salt or sea-salt may be used in addition to waste salt for mixing brine, provided it contains no minerals injurious to the subsequent processes.

Another apparatus produces a liquid six times stronger, intended for use in steam laundries.

All the apparatuses can be connected with a dynamo already in use for electric lighting, or any other electrical source of supply.

For further particulars apply to W. R. B. Lockie, 17A, South Castle Street, Liverpool, Agent for Great Britain.

THE
SOLUBILITY OF MANGANOUS SULPHATE.*

By THEODORE WILLIAM RICHARDS
and
FRANK ROY FRAPRIE.

THE solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell (*Journ. Phys. Chem.*, 1900, iv., 637), and the present paper is written to confirm in some measure the results of his work. He was able to disprove, by well considered experiment, the less recent work of Linebarger (*Am. Chem. Journ.*, 1893, xv., 225), who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly acknowledged when it is supported, hence the publication of the present paper.

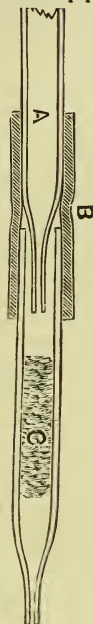
The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time. (A brief statement of the scope and object of this work will be found in *Proc. Amer. Assoc. Adv. Sci.*, 1898, 213).

It was soon found that a much higher temperature was necessary to drive off the water of crystallisation of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least one molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapour. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half-an-hour at 350° in an air-bath. In this respect the substance reminds one of cupric sulphate (Richards, *Proc. Amer. Acad.*, 1891, xxvi., 240). The amount thus retained does not much exceed the tenth of a per cent, and the effect upon Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a carefully watched naked flame, and applied after drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0.2 m.grm. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a

* Presented to the American Academy of Arts and Sciences, March 13, 1901. From the *American Chemical Journal*, xxvi., No. 1.

sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder (Schroder, *Zeit. Phys. Chem.*, 1893, xi., 454; Noyes, *Ibid.*, 1892, ix., 606; for details see Richards and Faber, *Am. Chem. Journ.*, 1899, xxi., 168, and *CHEMICAL NEWS*, xxix., 198). The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analysed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van't Hoff's laboratory (van't Hoff and Meyerhoffer, *Zeit. Phys. Chem.*, 1898, xxvii., 79). A diagram of the pipette is appended. The



FILTERING PIPETTE.

The filtering attachment, filled with cotton-wool ("absorbent cotton," c), is temporarily attached to the jet, A, of a 5 c.c. pipette by means of the rubber tube, B.

cotton was necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.

After filling the pipette and quickly removing the rubber filtering-jet attached to it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated, and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained:—

The Solubility of $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ at 25° .

No. of determination.	Time of saturation. Hours.	Weight of solution. Grms.	Weight of MnSO_4 . Grms.	MnSO_4 for 100 grms. water.
1.	6	5.0342	1.9849	65.09
2.	6	6.3405	2.4947	64.89
3.	8	4.4318	1.7470	65.07
4.	8	5.2465	2.0656	64.94
Average..				64.99
5.	48	3.4514	1.3622	65.20
6.	72	3.5349	1.3947	65.17
Average..				65.19

Cottrell found 64.78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only two and one-fifth hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded below:—

The Solubility of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ at 30.15° and 35.0° .

No. of determination.	Temperature. Hours.	Time of saturation. Hours.	Weight of solution. Grms.	Weight of MnSO_4 . Grms.	MnSO_4 for 100 grms. water.
7.	30.15°	4	4.3125	1.7215	66.44
8.	30.15°	4	5.7567	2.2943	66.27
9.	30.15°	4	4.5992	1.8339	66.32
10.	30.15°	4	5.2322	2.0894	66.48
Average..					66.38
11.	35.0°	13	3.7009	1.5007	68.21
12.	35.0°	14.5	2.7854	1.1296	68.22
Average..					68.22

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4.3 molecules of water for each MnSO_4 , but it was, nevertheless, probably the designated hydrate containing included mother liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from Determinations 11 and 12 contained 4.03 molecules of water.

The results at 30.15° , giving an average of 66.38, correspond almost exactly with Cottrell's figure, 66.43 at 30° ; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67.87, and ours, 68.22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case; and the higher figures, other things being equal, would have been accepted as the more accurate.

While this may be true, the recent work of Ostwald (*Zeit. Phys. Chem.*, 1900, xxxiv., 495) on the solubility of powders and the surface-tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapour-tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation (for example, see "Ostwald's Physico-chemical Measurements," Walker, Macmillan, 1894, p. 176). In view of Ostwald's newer work, it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it would simply hasten the speed of attaining saturation; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ attained a concentration of 57.41 grms. in 100 grms. of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72.5 to 62.3

grms. per 100. The solubility found after twenty-seven hours, when both methods gave the same result, was 58.32, or 0.91 grm. more than the first and 4 grms. less than the second figure.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Everyone will agree with Ostwald in deciding that the solution-tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermostat, would perhaps be the safest apparatus, although complete saturation would require much time (Richards, *Amer. Chem. Journ.*, 1898, xx., 189).

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty; but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25° with both or either hydrate to yield 40.1 grms. of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Continued from p. 146).

Lunge-Trillich or Seyler Method (continued).

THE essential details of the Seyler process are as follows:—

The free carbonic acid is determined by placing 100 c.c. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0.05 or 0.02 normal solution may be used), stirring carefully and thoroughly until a faint permanent pink colour is obtained.

The following precautions have been found desirable if accurate results are to be expected:—

1. The titration can conveniently take place in a short Nessler cylinder. The writers used a tube approximately 18 c.m. long by 3 c.m. in diameter, graduated for 50 and 100 c.c. The stirring rod used was bent at its lower end into the form of a circle, and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there was in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly, and the strong pink colour formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed. When the colour remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate, and with water which has been thoroughly boiled and cooled out of contact with the air. The exposure of this solution to the air should be avoided as much as possible, as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 c.c. for the titration, especially if 0.02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process (J. W. Ellms, *Journ. Amer. Chem. Soc.*, xxi., 359), is well known, and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed; or, in other words, a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink colour produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined, and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles upon which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties, and can be easily and quickly carried out. Approximately 0.02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulæ for calculating the results, which simplifies the work somewhat. If results are obtained with 100 c.c. of the sample and the reagents employed are 0.02 normal, the following formulæ express the results in parts per million:—

I. For waters acid or neutral to phenolphthalein:—

Free carbonic acid	= 4.4 p
Fixed or half-bound carbonic acid..	= 4.4 m
Volatile carbonic acid	= 4.4 ($m + p$)
Total carbonic acid	= 4.4 ($2m + p$)

p = c.c. 0.02 normal sodium carbonate solution required to produce a pink colour with phenolphthalein in 100 c.c. of the water; and

m = c.c. 0.02 normal sulphuric acid solution required to obtain the end-point with methyl-orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein:—

Fixed carbonic acid	= 4.4 m
Half-bound or volatile carbonic acid	= 4.4 ($m - 2p'$)
Total carbonic acid	= 4.4 ($2m - 2p'$)

m = c.c. 0.02 normal sulphuric acid solution required to obtain end-point with methyl-orange or lacmoid in 100 c.c. of the sample.

p' = c.c. 0.02 normal sulphuric acid required to discharge the pink colour produced by phenolphthalein in 100 c.c. of the sample.

* *Journal of the American Chemical Society*, xxiii., No. 6.

There is a third case in which free carbonic acid might exist in a solution containing free mineral acid, and for which Seyler has given a method with its corresponding formulæ for calculating the results. But such a condition would seldom be found in natural waters, and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method, and which in good work ought not to exceed 1 to 2 parts per million.

(To be continued).

THE DISSOCIATING POWER OF DIFFERENT SOLVENTS.*

(A SUMMARY).

By HARRY C. JONES.

Concluded from p. 146).

Mixed Solvents.

Hydrogen Dioxide and Water.—The dissociating power of a mixture of hydrogen dioxide and water has not yet been measured, but Calvert (*Ann. der Phys.*, i., 483), has found that the dielectric constant of such mixtures is greater than that of pure water. He employed the beautiful method of Drude, and from the dielectric constant of the mixture he calculated the dielectric constant of pure hydrogen dioxide to be 92.8 at 18°. The dielectric constant of pure water at this temperature is, according to Drude, 81.

J. J. Thomson (*Phil. Mag.*, xxxvi., 320), pointed out, as has already been mentioned, that there is probably a very close relation between the dielectric constants of solvents and their dissociating power. We shall see that while the two are not proportional, there is undoubtedly a qualitative relation between them. It is therefore very probable that the dissociating power of hydrogen dioxide is greater than that of water. This would not be very surprising, since many of the properties of hydrogen dioxide are simply the properties of water intensified. Work on this problem is now in progress in this laboratory.

Mixtures of Water and the Alcohols.—A number of experimenters have worked with mixtures of water and one or another of the alcohols. We should mention the work of Lenz (*Mem. de l'Acad. de St. Petersburg*, [7], xxx., 1881), Stephan (*Wied. Ann.*, xvii., 673), Kerler ("Dissertation," Erlangen, 1884), Kablukoff (*Zeit. Phys. Chem.*, iv., 432), Carrara (*Gazz. Chim. Ital.*, xvi. 1), Schall (*Zeit. Phys. Chem.*, xiv., 701), and Arrhenius (*Zeit. Phys. Chem.*, ix., 487). Quite an elaborate investigation on the conductivity of electrolytes in mixtures of water and ethyl alcohol, was carried out by Wakeman (*Zeit. Phys. Chem.*, xi., 49). His work had to do chiefly with the organic acids in mixtures of these solvents containing varying amounts of alcohol. The results showed that the conductivity became gradually smaller as the amount of alcohol present became larger and larger—just as would be expected from the relative conductivities in these two solvents.

But results of a very different character were obtained by Zelinsky and Krapin (*Zeit. Phys. Chem.*, xxi., 35) in mixtures of methyl alcohol and water. It will be re-

membered that electrolytes in methyl alcohol conduct, in general, to a much smaller degree than in water; yet certain salts were found to have greater conductivity in pure methyl alcohol than in a mixture of 50 per cent methyl alcohol and 50 per cent water. This is shown by the following table, taken from the work of Zelinsky and Krapin (*Zeit. Phys. Chem.*, xxi., 49):—

Potassium Bromide.

	Water.	Methyl alcohol.	Methyl alcohol, one-half; water, one-half.
v.	$\mu v.$	$\mu v.$	$\mu v.$
16	123.1	—	59.82
32	127.5	69.02	62.46
64	130.5	76.70	65.36
128	132.9	83.60	67.11
256	136.4	88.96	69.26
512	140.2	93.26	70.53
1024	143.4	97.25	—

Ammonium Iodide.

v.	$\mu v.$	$\mu v.$	$\mu v.$
16	125.4	72.24	62.63
32	129.6	78.74	65.04
64	133.4	85.0	67.48
128	135.9	91.14	69.28
256	138.7	96.20	70.34
512	141.3	100.6	71.12
1024	143.7	104.7	71.57

It is impossible at present to say what these surprising and very remarkable results mean. They are confirmed by the work of Kerler and of Carrara.

Similar results were obtained by Cohen (*Zeit. Phys. Chem.*, xxv., 31) with ethyl alcohol and water, but only when the mixture contained very little water and at dilutions which were quite large, as is shown by the following table:—

Potassium Iodide.

	Pure alcohol.	Eighty parts alcohol and twenty parts water.
v.	$\mu v.$	$\mu v.$
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

The conductivity in the mixture is the greater until a dilution of 512 litres is reached, when the conductivity in the pure alcohol becomes greater than in the alcohol containing 20 per cent of water.

Cohen found, however, for most substances that the presence of water in the alcohol increased the molecular conductivity, as we would expect.

Conclusions from the Work thus far Done.

An examination of the work described in this review will show that different solvents have very different ionising power. With the possible exception of hydrogen dioxide, water is the strongest ioniser; next to this comes formic acid. Of the more common solvents, methyl alcohol dissociates to a much greater degree than ethyl alcohol. Indeed, it is true, in general, that in an homologous series of solvents the lower members have the greater dissociating power.

It has already been mentioned that attempts have been made to discover relations between the ionising power and other properties of a solvent. Thomson's theory that the dissociating power and the dielectric constants of solvents should stand in very close relation to each other, undoubtedly contains a large element of truth. Those solvents which have the largest dissociating power have, in general, the largest dielectric constants. A number of independent investigations have shown that these two properties are not proportional.

* *American Chemical Journal*, xxv., No. 3.

The suggestion of Dutoit and Aston that there is a connection between the amount of association of the molecules of a solvent and its power to ionise electrolytes, undoubtedly contains much truth. Thus, the molecules of water are associated to a greater extent than those of any other liquid, as Ramsay and Shields have shown. The molecule of liquid water at ordinary temperatures is $(H_2O)_4$. Similarly, the alcohols and other strongly dissociating solvents show considerable association of their molecules.

It will probably be shown that the dissociating power of a solvent is not a function of any one physical or chemical property of the substance, but of them all. Or, perhaps, more accurately expressed, all the properties of a substance are a function of the energy relations which obtain in that substance, and ionising power is simply one of these properties.

The conclusion from this work which is of chief importance for pure chemistry is that ions are almost always present when chemical reaction takes place. When the number of solvents which can effect ionisation to some extent is considered, and the fact that heat and possibly pressure can dissociate molecules, it will be seen that there is scarcely a chemical reaction in which ions as well as molecules are not present. The question then arises—Which causes the reaction, the ions or the molecules? This can be answered by excluding ions and then observing whether chemical reaction takes place or not. This has been done, with the following results:—Hydrochloric acid gas, dried and dissolved in dry chloroform, does not conduct the current, and is, therefore, not dissociated. Under such conditions it will not decompose carbonates. Liquid hydrochloric and sulphuric acids, when free from water, will not turn litmus red. Dry hydrochloric acid gas and dry ammonia gas do not react to the slightest extent. Still more surprising perhaps, is the fact that sulphuric acid free from water will not react upon dry metallic sodium. Special precautions must be taken, of course, in all such cases to remove every trace of moisture.

The above examples might be largely increased, but these suffice to show the chemical inertness of molecules. We are now in a position to say that most chemical reactions, if not all, are reactions between ions, and molecules as such do not enter into the reactions at all. As the reactions proceed and the ions already present are used up, the molecules are gradually dissociated and furnish new ions which then enter into the reaction. The chemistry of atoms and molecules has thus given place to the chemistry of ions.

NOTICES OF BOOKS.

Chemical Lecture Experiments. By FRANCES GANO BENEDICT, Ph.D., Instructor in Chemistry in Wesleyan University. New York: The Macmillan Company. London: Macmillan and Co. 1901.

THE object of this book is to furnish teachers of chemistry with a selection of lecture experiments that can be made quickly, and not needing costly or complicated apparatus. The book will be of value to any who have a number of classes to prepare for, and limited time. It is full of devices for producing striking effects with simple commonplace apparatus. The chapters on the preparation of gases are good, and include many simple though little known methods. In some cases there seems to be a tendency to make rather too much of the effect. For instance, to show the combustion of charcoal, finely powdered charcoal is heated to redness, and poured into a jar of oxygen, the hands and face of the operator being protected with gauntlets, &c.!

We are afraid that in this case the truth that it is desired to demonstrate would be swamped in the effect. However,

the book does not claim to be a text-book, and the teacher who makes use of it must use his own discretion in selection.

To facilitate the preparation of the experiments a list of chemicals and apparatus required has been appended, in no case demanding anything not ordinarily found on a lecture table. The book is well illustrated and indexed.

RESEARCH FELLOWSHIP IN CHEMISTRY.

THE RESEARCH FELLOWSHIP founded by the LEATHERSELLERS' COMPANY for the encouragement of Higher Research in Chemistry in its relation to Manufactures, tenable at the City and Guilds Central Technical College, being vacant, the Executive Committee of the City and Guilds of London Institute is prepared to consider applications. The Grant made by the Company to the Institute for this purpose is £150 a year. Copies of the scheme under which the Fellowship will be awarded may be had from the HONORARY SECRETARY of the Institute, Gresham College, 91, Basinghall Street, E.C.

CITY OF LONDON COLLEGE, WHITE STREET, MOORFIELDS, E.C.

MICHAELMAS TERM commences SEPTEMBER 30th.

EVENING CLASSES in CHEMISTRY, BOTANY, GEOLOGY, BIOLOGY, and all Science subjects. Well equipped Laboratories for Practical work. Low fees. Prospectus gratis on application to DAVID SAVAGE, Secretary.

CITY AND GUILDS TECHNICAL COLLEGE, FINSBURY, LEONARD STREET, E.C.

SESSION 1901-1902.

EVENING CLASSES.

THE new SESSION begins on MONDAY, SEPTEMBER 30th, at 6 p.m. Lectures and Laboratory Work, Mechanical and Electrical ENGINEERING, Industrial and Technical CHEMISTRY, APPLIED ART, including Lectures on Domestic Furniture and Practical Instruction in Enamels and Art Metal Work, DRAWING, PAINTING, &c. The Programme may be obtained at the College, Leonard Street, Finsbury, or at the Head Office of the City and Guilds of London Institute, Gresham College, E.C.

JOHN WATNEY,
Honorary Secretary of the Institute.

GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.

DEPARTMENT OF CHEMISTRY.

EVENING CLASSES, providing complete Courses of Instruction in various branches of Pure and Applied CHEMISTRY, are held at this Institute under the direction of Mr. ARTHUR LAPWORTH, D.Sc.(Lond.), F.I.C., &c. The Courses of Lectures and Practical Laboratory teaching are suitable for Students desiring to qualify in Chemistry at the Examinations of the London University, the Pharmaceutical Society, the Board of Education, and other public bodies. The equipment of the Chemical Laboratories has been considerably augmented and exceptional facilities are offered to advanced Students who desire to engage in Chemical Research Work during the Day or Evening. The new SESSION commences on SEPTEMBER 23rd. For further particulars apply to the Secretary.

J. S. REDMAYNE, B.A., Secretary.

SOUTH-WESTERN POLYTECHNIC MANRESA ROAD, CHELSEA, S.W.

Principal—HERBERT TOMLINSON, B.A., F.R.S.
Head of Chemical Section—J. B. COLEMAN, A.R.C.S., F.I.C.

THE DAY CHEMICAL and METAL-LURGICAL DEPARTMENTS will re-open MONDAY, SEPTEMBER 30th. The full Chemical Course, which occupies three years, is arranged for intending Analysts, Industrial Chemists, Assayers, and others. Inclusive Fee for the Session, £15. The Laboratories are also available for occasional Students. For further information see Day Prospectus, price 3d. per post.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2184.

ON THE CHEMICAL AND BIOLOGICAL
CHANGES OCCURRING DURING THE
TREATMENT OF SEWAGE BY THE SO-CALLED
BACTERIA BEDS.*

By Professor LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.C.S., F.I.C.

It is generally assumed that the so-called "bacteria beds" act as oxidising agencies absorbing oxygen from the air during their periods of rest, and subsequently transferring it to the constituents of the sewage when the beds are filled with this latter, the transfer being effected by micro-organisms which have established themselves on the surface of the material with which the beds are filled.

It also appears to be generally taken for granted that the micro-organisms mainly concerned in the purification process are the nitrifying organisms. Hence if these views are correct, the effluent from the bacteria beds should contain nitrates and nitrites equivalent in amount to the unoxidised nitrogen which disappears during the treatment. But on examining the results obtained by chemists in investigation on sewage purification it will be found that comparatively small amounts of nitrate and nitrite are produced in relation to the unoxidised nitrogen disappearing.

The following figures are taken (or have been calculated) partly from results given in the Manchester Report of the Rivers Committee, January 22nd, 1900, Table I., the Leeds Report on Sewage Disposal, December, 1898, Table I., and partly from the Table (p. 68), given in Dibdin's book on the "Purification of Sewage and Water."

	Nitrogen disappearing as "free" and "albumenoid" ammonia.	Nitrogen found in the effluent as nitrate and nitrite after double contact with the bacteria beds.	
	Grains per gallon.	Grains per gallon.	Percentage on nitrogen disappearing.
Manchester ..	1.634	0.636	39
Sutton	7.185	1.100	15
Leeds	1.528	0.11	7

It is quite evident, therefore, that a considerable portion, and in most cases the greater part, of the unoxidised nitrogen which disappears must be got rid of in some other form, and the question arises as to how this may occur. In all probability there are two—and only two—alternative ways in which the nitrogen can be lost, viz. :—

1. It may escape in the gaseous state as free nitrogen, or possibly as oxides of nitrogen.

2. It may pass into the tissues of animals or vegetables, the former of which may escape from the bacteria beds, and the latter (and possibly the former also) may remain permanently in the beds.

In other words, there may be either a chemical or a biological explanation, or both together.

Chemical Explanation.—In an investigation on the effects of double contact with bacteria beds on screened and settled sewage the authors made analyses of the dissolved gases present, both in the original sewage and in the effluent from both beds, the samples being collected in such a manner that they did not come into contact with the air.

The general results of these analyses were as follows :—1. Practically no oxygen was present, either in the sewage or effluents. 2. The effluent from first contact

always contained considerably more carbonic anhydride than the original sewage, and with two exceptions the effluent from second contact also contained an excess of that gas. 3. In eleven out of twelve series of analyses the quantity of nitrogen in the effluent was in excess of that present in the original sewage, and, generally speaking, it was in larger excess in the effluent from double contact than in that from single contact.

As the first six series of analyses only were made under exactly the same conditions, the authors find that, taking them as the basis of calculation, on the average the excess of nitrogen in the effluent from second contact over that present in the sewage amounted in weight to 0.272 part per 100,000, while the loss of unoxidised nitrogen which had occurred in the sewage (by Kjeldahl's process) amounted to 2.2 parts, or that 12 per cent of the nitrogen lost from the sewage during purification was thus accounted for, while in one particular case it amounted to 31 per cent.

In all probability only a fraction of the free nitrogen actually evolved would be retained by the effluent, the rest escaping into the air.

Biological Explanation.—As regards the possibility that nitrogen is lost biologically, i.e., is absorbed into the tissues of animals or plants which feed on the sewage, there can be no doubt that a portion does escape in that way. The bacteria beds at Belfast, and elsewhere, swarm with minute insects (*Podura aquatica*). These, escaping in myriads, often form a thick layer on the surface of the effluent, which looks like soot. There can be no question that in thus escaping these animals carry with them some of the nitrogenous constituents of the sewage which they have devoured, but as yet the authors have formed no estimate of the quantity so removed. There are also species of worms always present in the bacteria beds in considerable numbers which no doubt also feed on the sewage.

SULPHURIC ACID AS A TYPHOID
DISINFECTANT.*

By SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C.

THE comparatively small quantities of sulphuric acid which are necessary to inhibit the growth of *Bacillus typhosus* in water has long been known, and quite recently the author, in conjunction with Dr. Parkes (Parkes and Rideal, *Epidemiological Society's Transactions*, 1901, xx.), has suggested the use of acid sulphate of soda for sterilising potable water amongst armies in the field and for colonists when away from satisfactory water supplies.

The sodium bisulphate is to be preferred for this purpose, as it is more portable than sulphuric acid. Comparative experiments with sodium bisulphate, tartaric acid, citric acid, and nitro-hydrochloric acid and sulphuric acid show that the organic acids are less efficient than the mineral acids for this purpose, and that nitrohydrochloric acid of equal acidity to sulphuric acid is superior, owing no doubt to the fact that the action due to the acid is supplemented by the potential free chlorine that is present in such a mixture.

In our experiments, the following results were obtained:—

750 c.c. of Tap-water Infected with One Drop of a twenty-four hour Broth Culture at 37° C. of *Bacillus typhosus*.

Agar plate cultures made with 1 c.c. of mixture.	Acidities per pint required to kill, in c.c. N/10 acid.		
	In five minutes.	Fifteen minutes.	Forty-five minutes.
Sodium bisulphate ..	84	—	42
Tartaric acid	—	86	—
Citric acid	—	203	—
Nitro-hydrochloric acid.	—	31.25	—
Sulphuric acid	—	33	—

* Read before the British Association (Section B), Glasgow Meeting, 1901.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

For sterilising water in bulk in case of typhoid outbreak, or in isolation hospitals, sulphuric acid being the cheapest reagent is to be preferred, and possesses advantages over methods of heat sterilisation which lead one to imagine that its more general use for this purpose would be advantageous. The alkalinity of sewages, and that present in most drinking waters, neutralises a certain amount of acid, and therefore an additional amount based upon the alkalinity of the infected water has to be allowed for. It is known, however, that sewages have an alkalinity which seldom falls below 20 parts per 100,000 or rises above 60 parts per 100,000 of sulphuric acid; in other words, the addition of 3 grms. of sulphuric acid per gallon is sufficient for neutralising any possible alkalinity in a sewage or drainage water from an infected area. As the quantity of acid required for inhibiting the growth of the typhoid organism can be taken at 1 grm. per gallon, it follows that an addition of 4 grms. of sulphuric acid per gallon is sufficient for ensuring the death of the typhoid organism in the drainage waters from an isolation hospital or other infected area. It further follows that the free acidity produced in this way would be speedily neutralised when such water becomes mixed with any fresh sewage which has not been similarly treated, and as the infected sewage must always represent a very small proportion of the total drainage to be dealt with, this method of ensuring the absence of typhoid in drainage waters is satisfactory in practice. Although there is some evidence to show that the organism does not thrive in sewage or on bacterial beds, it seems desirable that a method of ensuring the absence of the organism in the sewage before reaching the sewage disposal works is to be desired, and the author submits the above as a method of solving this problem.

THE NOMENCLATURE OF THE IONS.*

By JAMES WALKER, F.R.S.

ANYONE who has had to teach the theory of electrolytic dissociation must have found himself hampered by the want of a systematic and consistent nomenclature for the material of the the ions as distinguished from the particles themselves. Thus, whilst we may speak of hydrogen ions, chloride ions, or sulphate ions, meaning thereby the particles or molecules supposed to exist in aqueous solution, we have no systematic names for the substances which these supposed molecules constitute.

A basis for such a nomenclature was supplied by Faraday, who used the termination *ion* in conjunction with the stems of the ordinary chemical names. Thus, *sulphion* was the negative ion or radical of the sulphates, *nitron* of the nitrates, and so on.

It is evident, however, that in the form used by Faraday these names are inadequate. *Sulphion* might be derived from sulphate, sulphite, or sulphide; there is nothing in the name to indicate which. On the Continent, and even in this country, the names *sulphation*, *sulphition*, and *sulphidion* have been proposed to overcome this difficulty. But it is obviously doing violence to the principles of English pronunciation (such as they are) to speak "sulphation" otherwise than as a rhyme to "relation," or "sulphition" otherwise than as a rhyme to "condition." The terminations *ation* and *ition* must be discarded unless we are to make our chemical terminology even more arbitrary and confusing than it is at present.

The proposals which I make for naming the positive and negative radicals of salts, acids, and bases considered as ions are as follows:—

For positive radicals or kations the name is obtained by adding the termination *ion* to the stem, and prefixing where necessary a Greek numeral to indicate the electrical charge or valency of the radical. Thus, if we use with

Ostwald a dot to express unit positive charge, we have for some typical kations:—

Hydriion	H ⁺
Sodion	Na ⁺
Ammonion	NH ₄ ⁺
Potassion	K ⁺
Calcion	Ca ⁺⁺
Barion	Ba ⁺⁺
Monomercurion	Hg ⁺ (in mercurous salts)
Dimercurion	Hg ⁺⁺ (in mercuric salts)
Diferriion	Fe ⁺⁺ (in ferrous salts)
Triferriion	Fe ⁺⁺⁺ (in ferric salts)
Chromion	Cr ⁺⁺⁺

For negative radicals or anions the name is obtained by substituting, in accordance with the following table:—

Termination of salt radical.	Termination of anion.
—ate	—anion
—ite	—osion
—ide	—idion

These terminations for the anions are all compound, and easily distinguishable from the simple termination of the kations. The termination *anion* was selected because it begins with the same vowel as *ate*, and is for the rest self-explanatory. The termination *osion* was chosen because it indicates connection with the *ous* acids from which the *ites* are derived.

The following are some typical anions, each dash attached to the formula indicating unit negative charge:—

Hydroxidion	OH ⁻
Sulphidion	S ⁻
Sulphosion	SO ₃ ⁻
Sulphanion	SO ₄ ⁻
Chromanion	CrO ₄ ⁻
Carbanion	CO ₃ ⁻
Orthophosphanion	PO ₄ ⁻
Metaphosphanion	PO ₃ ⁻
Chloridion	Cl ⁻
Chloranion	ClO ₃ ⁻
Hypochlorosion	ClO ⁻
Acetanion	C ₂ H ₃ O ₂ ⁻

Anions, such as H₂PO₄⁻ and HPO₄⁻ (from NaH₂PO₄ and Na₂HPO₄), may be named *dihydrophosphanion* and *hydrophosphanion* respectively. The anion HCO₃⁻ of the bicarbonates would be thus called *hydrocarbanion*.

The complex anion Ag(CN)₂⁻ from potassium-silver cyanide would, on the above system, receive the name *argenticyanidion*; the anion AgS₂O₃⁻ *argentithiosulphanion*, and so on. If the system is consistently applied, there is no difficulty in finding names for the ions if we have a name for the salt from which they are derived.

The only instances in which the system might lead to any ambiguity are those complex kations, in which the Greek numerals are used in the ordinary chemical manner, and might possibly be confused with the prefixes indicating charges. But as these prefixes are required in the second sense practically for simple kations only, there is no real risk of ambiguity or confusion.

The system, although devised for English, might, with appropriate alterations, be easily adapted to other languages.

The use of the above compound names in the molecular as opposed to the substantial sense should be carefully avoided. Thus, a *chloridion* or *chloridions* (to indicate *chloride ions*) should never be used. We should no more speak of a *chloridion* or *chloridions* than of a *chlorine* or of *chlorines*. If we wish to indicate the particles we ought to say *chloride ions*, as formerly, or *chloridion molecules*.

It may seem to some that the matter here discussed is trivial, but it appears to me that if a system such as I have proposed had been adopted when the ionisation hypothesis was first brought forward a great deal of mis-

* Read before the British Association (Section B), Glasgow Meeting, 1901.

apprehension might have been avoided. To say that sodium chloride when dissolved in water is partially decomposed into the substances *sodium* and *chlorine* is altogether misleading; to say that it is partially decomposed into the substances *sodium* and *chloridion* is quite a different statement, and one with a clear and definite meaning. Sodium is no more sodium than oxygen is ozone, or graphite diamond.

University College, Dundee.

THE MINUTE STRUCTURE OF METALS.*

By G. T. BEILBY.

MICROSCOPIC examination of metallic surfaces produced by breaking, tearing, or filing, by rolling, drawing, hammering, or polishing, has shown that the metals, as they are ordinarily met with, appear in two forms:—

- (a) As minute scales or "spicules."
- (b) As a transparent glass-like substance.

These two forms of "metal substance" occur in all the metals examined, and, taken together, they do not appear to depend in any way on the particular thermal or mechanical treatment to which the metal has been subjected, nor upon the greater or less mass of the particular piece of metal examined. Their existence is, therefore, to a great extent, independent of the conditions which determine the particular crystalline structure in metals and alloys.

In form (a) the scales or "spicules" do not vary much in size in the different metals examined, which include among their number representatives of most of the great groups. The diameter of the scales is estimated to range from $\frac{1}{100}$ to $\frac{1}{50}$ of a millimetre. Their thickness has not yet been measured, but they can be seen by reflected light, when their thickness is certainly less than $\frac{1}{1000}$ of a millimetre.

Form (b) is seen as a transparent glass-like film on metal surfaces which have been exposed to certain forms of pressure. In the transparent form the metals have their characteristic colours by transmitted light; for instance, gold is green, iron is blue.

The scale form (a) passes into the transparent form (b) when the metal is pressed or hammered upon a hard polished surface. The same effect takes place when a mirror-like polish is produced by ordinary methods. Files or cutting tools, in passing over the surface or through the substance of metals, leave the cut or scraped surface covered with a more or less continuous film of transparent metal. All polished metallic surfaces are covered with a thin layer of transparent metal like a lacquer or enamel.

By suitable treatment, a coating of transparent metal can be formed of varying degrees of thickness, so that, by reflected light, scales can be seen more or less deeply embedded in the transparent coating. The light from the deeper scales shows the characteristic colour of the metal. In some cases the colour of the coating, as seen by the microscope, is so intense that no reflected light reaches the surface.

Attempts have been made to measure the thickness of the transparent film by focussing for its upper and lower surfaces, or for the upper surface, and for scales embedded in the film, and measuring the movement of the microscope between these points. As the measurements appear to give rather exaggerated results their publication is held over for the meantime.

The transparent metal (b) passes back into the scale form (a) under the influence of certain kinds of mechanical and chemical treatment.

The metals already examined include gold, silver, platinum, cobalt, nickel chromium, iron, copper, lead,

bismuth, antimony, tin, cadmium, magnesium, aluminium, zinc, and sodium.

The highly crystalline metals, such as antimony, bismuth, and zinc, exhibit the same features as the softer and more malleable metals. The crystalline faces and cleavages are covered with a film of transparent metal, while scales are distinctly seen in fractures at right angles to the cleavage planes. Certain ores show similar appearances.

The zinc and tin alloys of copper show the same minute structure and appearances as the pure metals.

The persistence of these minute scales or "spicules" under all kinds of mechanical and thermal treatment, the remarkable uniformity of their size and appearance in metals of all the leading groups, their disappearance into the transparent form, and their re-appearance again, apparently unchanged in size or otherwise, seem to afford fair ground for the conjecture that they are, in some way, definite units in the structure of metals.

ALUMINIUM-TIN ALLOYS.*

By W. CARRICK ANDERSON, M.A., D.Sc.,
and
GEORGE LEAN, B.Sc.

THIS investigation was undertaken to ascertain, with some definiteness, the general properties of the alloys of aluminium and tin, and particularly the cause of the peculiarity, first pointed out by Riche (*Journ. Pharm. Chem.*, 1895, I, v.), that the alloy containing 25 per cent aluminium evolves hydrogen freely when placed in water. This property was found to belong, not only to the particular alloy in question, but to the whole series, whether cast or annealed.

From the determinations of the cooling curves it is shown that tin dissolves in aluminium, but that in the case of alloys containing more than 10 per cent tin a second break in the cooling curve takes place at 232°C ., indicating an excess of tin (Gautier, *Comptes Rendus*, 1896, cxxiii., 109). Microphotography was also employed to show the structure of the alloys in the cast and annealed condition. The amounts of hydrogen evolved from the several alloys, cast and annealed, were found to stand in no simple relation either to the weights of the constituent metals present, or to the depression in the aluminium melting-point.

From microscopic examination of water-corroded plates the conclusion is arrived at that contact action between the tin and the stanniferous aluminium is mainly responsible for this spontaneous oxidation.

ON THE POSSIBILITY OF SYSTEMATIC ERROR IN PHOTOGRAPHS OF A MOVING OBJECT.†

By ARTHUR R. HINKS.

As a preliminary to the discussion for a determination of the Solar Parallax of a series of photographs of the planet Eros, made last winter by the author at Cambridge Observatory, it was essential to assure one's self that no systematic error was produced by the motion of the planet during the exposure (generally three or two minutes). Two series of plates were taken—(a) with stars fixed and planet trailing; (b) with planet fixed and stars trailing.

It is easy to imagine how such an error might arise. Owing to atmospheric disturbance, the image of a star during exposure is buzzing about on the plate around its

* Read before the British Association (Section B), Glasgow Meeting, 1901.

† Read before the British Association (Section A), Glasgow Meeting, 1901.

* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

mean position. The developable image is thereby enlarged, and a larger area still on the sensitive film is prepared for decomposition, just as very sensitive plates are prepared by preliminary exposure to faint light. Consequently, if the image is trailing on the plate, it is trailing on to a surface already prepared to the point of decomposition, and it seems possible that the centre of the developed image might therefore be in advance of its true place.

The author shows (1) that if such an effect were independent of the magnitude of the star, the two series (a) and (b) would be rigorously comparable with one another, but each would give the place of the planet with respect to the stars ahead of its true position by the same amount; (2) that it is almost certain, however, that the effect would depend on the brightness of the star; (3) that a comparison of the two series of plates gives no evidence of the existence of a differential effect varying with the magnitude of the star; and (4) that the absolute error is therefore probably also insignificant.

UTILISATION OF NASCENT CARBON DIOXIDE AS A CHEMICAL REAGENT.

By H. NICHOLSON.

IN the manufacture of chemicals carbon dioxide plays a somewhat important part. Up to the present time conjunction in the form of an alkaline carbonate or bicarbonate has been the usual manner of conveyance, inasmuch, of course, that any acidity of suspending liquid prevents the formation of carbonates.

During some experiments on a fairly large scale with explosive mixtures of air and inflammable gases, burning them in a specially constructed burner under water, it occurred to me that the CO_2 (the product of the combustion)—formed, as it is, in direct contact with, and under the surface of, the water—might possess increased activity at the moment of its generation, and decompose some salts of metals having insoluble carbonates and in which it is in ordinary circumstances necessary to bring about decomposition with alkaline carbonates.

My first experiments have been on borate of calcium.

On suspending finely-ground borate of calcium in water, and boiling with the flame of air and gas (producer gas), immersed and in actual contact with the liquid, decomposition occurs. Under ordinary circumstances boric acid decomposes calcium carbonate slowly, but in the presence of nascent CO_2 calcium carbonate is formed and boric acid goes into solution.

On withdrawing the burner, and so removing the influence of nascent gas, the free acid commences to decompose the CaCO_3 and re-form calcium borate. The effect of the burner is an interesting example of the influence of nascent gases on chemical equilibrium, and opens up a large field for research.

The combustion of gases under water and in actual contact is unique, presenting a new sphere of possibilities in chemical reactions.

THE ESTIMATION OF CARBONIC ACID IN WATER.*

By JOSEPH W. ELLMS and JAY C. BENEKER.

(Concluded from p. 159).

Comparison of the Three Methods on Waters containing Known and Unknown Amounts of Carbonic Acid.

THE comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these three methods. Solutions containing known amounts of free and half-bound carbonic acid were prepared by neutralising partially or wholly measured quantities of a 0.02 normal solution of sodium carbonate

with a 0.02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order that these bases might be present and thus produce an artificial water having approximately the same composition as natural waters.

The first table shows the amount of free carbonic acid obtained in a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the following tables in the sense in which it was defined in the first portion of this paper. Strictly speaking, in the absence of magnesium salts, where the use of ammonium chloride is unnecessary, the columns could have been headed "Pettenkofer method"; but, to avoid confusion, the definitions first given have been adhered to.

Table showing Free Carbonic Acid found in a Solution known to contain 44 Parts per Million.

No.	Trillich method. Parts per million.	Seyler method. Parts per million.
1	41.7	44.2
2	43.7	44.7
3	42.2	44.2
4	40.8	43.8
5	42.7	44.0
6	41.7	43.6
7	40.8	44.4
Average	42.0	44.0

When free and half-bound carbonic acid were present together in known amounts the following results were obtained:—

Table showing Free and Half-bound Carbonic Acid found in a Solution known to contain 8 Parts Free and 40 Parts Half-bound Carbonic Acid. (Free and Half-bound Acid equals 48 Parts Per Million).

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.	
		Free acid. Parts per million.	Half-bound acid. Parts per million.
1.	47.0	7.0	40.8
2.	46.1	6.2	41.3
3.	46.1	6.6	41.3
4.	47.0	7.0	41.3
5.	47.0	7.9	41.3
6.	45.0	7.9	41.3
7.	45.4	7.5	41.3
8.	46.1	7.9	40.8
9.	46.1	7.0	41.3
10.	46.1	7.9	41.3
Average	46.2	7.3	41.2

The following table shows the results obtained with these methods when the solution contained double the amount of free and half-bound carbonic acid as was present in the solution from which the figures in the preceding table were obtained:—

Table showing Free and Half-bound Carbonic Acid found in a Solution known to contain 16 Parts Free and 80 Parts Half-bound Carbonic Acid. (Free and Half-bound Acid equals 96 Parts per Million).

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method.	
		Free acid. Parts per million.	Half-bound acid. Parts per million.
1.	92.2	15.8	78.2
2.	91.0	14.5	81.1
3.	91.0	14.1	81.1
4.	90.5	14.5	80.2
5.	90.5	15.0	80.2
Average	91.0	14.8	80.1

* Journal of the American Chemical Society, xxiii., No. 6.

No attempt has been made in our work with Pettenkofer's and Trillich's methods to differentiate by titration (according to Trillich's method) the free carbonic acid from the half-bound. Assuming, however, that the half-bound acid in the above solution is, as shown by the average, 80·1 parts per million, then the free carbonic acid by Pettenkofer's or Trillich's method would be 91 parts minus 80·1 parts, or 10·9 parts per million.

In the following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid, and which also contained varying but known amounts of magnesium salts.

Table showing Free and Half-bound Carbonic Acid found in Solutions known to contain 4·9 Parts Free and 41·6 Parts per Million of Half-bound Carbonic Acid, and with Varying Amounts of Magnesium Sulphate. (Free and Half-bound Acid equals 46·5 Parts per Million).

No.	Magnesium sulphate present	Pettenkofer method. Free and half-bound carbonic acid.	Trillich method. Free and half-bound carbonic acid.	Seyler method.		
				Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.
		Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
1.	10	44·6	43·9	4·6	48·2	45·8
2.	10	43·1	43·9	—	—	—
3.	10	43·1	44·4	—	—	—
4.	20	41·5	45·6	4·3	41·2	45·5
5.	20	44·6	44·2	4·0	41·9	45·9
6.	40	44·6	43·3	4·0	42·6	46·6
7.	40	43·1	40·4	4·6	41·2	45·8
8.	40	46·0	40·4	—	—	—
Average ..		43·8	43·2	4·3	41·6	45·9

Assuming, as in the preceding tables, that the half-bound carbonic acid is on an average 41·6 parts per million in the above solution, then the Pettenkofer results indicate 2·2 parts per million of free carbonic acid and the Trillich results 1·6 parts per million.

Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table given below shows the results obtained on a sample of Ohio river water by the three different methods. This sample of water contained, by a gravimetric determination, 10 parts per million of magnesium oxide, equivalent to a correction to be applied to the Trillich figures of 11 parts per million.

Table showing Amount of Carbonic Acid found in Ohio River Water by the Three Methods.

No.	Pettenkofer method.	Trillich method.	Seyler method.		
	Free and half-bound carbonic acid.	Free and half-bound carbonic acid.	Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.
	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.
1.	14·9	15·4	0·6	16·2	16·8
2.	14·9	16·8	0·4	16·4	16·8
3.	13·4	16·1	0·4	16·2	16·6
4.	14·4	16·8	0·4	16·6	17·0
5.	14·4	16·8	0·6	16·6	17·2
6.	14·4	16·1	0·6	16·2	16·8
7.	13·4	16·8	0·4	16·4	16·8
8.	14·9	15·4	0·4	16·6	17·0
9.	13·2	16·8	0·4	16·6	17·0
Average	14·2	16·3	0·4	16·4	16·8

The following well-water was also examined, and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of magnesium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results:—

Well-water.

	Parts per million.
Lime (CaO)	378
Magnesia (MgO)	128
Sulphuric acid (SO ₃)	351

The free and half-bound carbonic acid were determined by the three volumetric methods, and the results obtained are shown in the following table:—

Table showing Amount of Carbonic Acid found in a Well-water by the Three Methods.

No.	Pettenkofer method.	Trillich method.	Seyler method.			
	Free and half-bound carbonic acid.	Free and half-bound carbonic acid.	Free carbonic acid.	Half-bound carbonic acid.	Free and half-bound carbonic acid.	
	Parts per million.	Parts per million.	Parts per million.	Parts per million.	Parts per million.	
1.	241	242·4	63·4	176·4	239·8	
2.	241	236·5	66·9	176·4	243·3	
3.	241	236·5	68·6	176·4	245·0	
4.	241	246·3	65·1	177·4	242·5	
5.	238	242·4	68·6	176·4	245·0	
Average		240·4	240·8	66·5	176·6	243·1

As would be expected, the variation in the above results is in some cases considerable, but the greatest difference is less than 10 parts per million, and the greatest variation from the mean of all the results is less than 5 parts per million.

The results of the above analyses were all obtained on waters which when cold reacted neutral or acid to phenolphthalein. There is one other class of waters which when cold react alkaline to phenolphthalein, and which, in consequence, require a modification of Seyler's method, as previously described. The number of waters belonging to this class does not seem to be at all large, and the writers have never examined but one water which showed this feature. Seyler states that pure sea-water is alkaline to phenolphthalein. He gives the following analysis:—

	Parts per million.
Free carbonic acid	0
Half-bound carbonic acid	44·0
Fixed carbonic acid	51·7
Total carbonic acid	95·7

He also states that he has found well-waters which, upon standing exposed to the air for some time, reacted alkaline to phenolphthalein, and that such waters contained considerable magnesium carbonate.

The writers have found that, at certain times, the Mississippi river water is alkaline to phenolphthalein. How long such periods last or at what seasons of the year they occur we have not had the opportunity to determine. It is quite probable that the so-called "alkali waters" of the Western plains would react alkaline to phenolphthalein, as they contain carbonates of sodium. It has been noted that water which has stood in the iron pipes of the laboratory for some time, will, when first drawn, react alkaline to phenolphthalein. This is due probably to the free carbonic acid and bicarbonates in the water reacting with the iron of the pipe to form carbonate of iron, and thus leaving in solution small amounts of normal calcium and magnesium carbonates.

The water examined by us which reacted alkaline to phenolphthalein was a mixed sample of Mississippi river water. The samples were taken during the month of September, 1900, opposite Quincy, Illinois. When examined it was found to give a strong pink colour with phenolphthalein. Its average approximate composition was as follows:—

	Parts per million.	
Lime (CaO)	35.6	equivalent to 63.5 parts CaCO ₃ .
Magnesia (MgO)	16.0	equivalent to 33.6 parts MgCO ₃ .
Sulphuric acid (SO ₃) ..	7.2	
Chlorine (Cl)	6.3	
Fixed carbonic acid (CO ₂)	39.8	equivalent to 90.4 parts when expressed in the form of calcium car- bonate.

From a consideration of these results, it is more than probable that the magnesium was present partly as normal magnesium carbonate (MgCO₃), and the calcium as calcium bicarbonate. Only a limited quantity of the sample was available for experimental purposes. The following table shows the average of the results obtained in determining the carbonic acid by the three volumetric methods:—

Carbonic Acid obtained in a Sample of Mississippi River Water.

	Parts per million.
Pettenkofer method—	
Free carbonic acid	0
Half-bound carbonic acid	0
Trillich method—	
Free carbonic acid	0
Half-bound carbonic acid	34.6
Seyler method—	
Free carbonic acid	0
Half-bound carbonic acid	35.4

Seven different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium hydroxide used up, and that, on an average, only 60 parts per million (expressed in terms of CaCO₃) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the ammonium chloride used was one factor which was instrumental in holding a portion of the carbonates in solution. Whether the dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state.

An artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:—

	Parts per million.		
	No. 1.	No. 2.	Average.
Pettenkofer method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	27.9	29.4	28.7
Trillich method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	31.6	31.6	31.6
Seyler method—			
Free carbonic acid	0	0	0
Half-bound carbonic acid	31.7	32.2	31.9

This water contained 11 parts per million of magnesium oxide, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they were in the river water.

Conclusions.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid," as determined on known amounts by this method, is, on an average, less than 1 per cent too low, and shows a possible range of less than ± 3 per cent. The accuracy of the

determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low, and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method, but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are, on an average, between 5 and 10 per cent too low. While Trillich's method gives more uniform results than Pettenkofer's, the figures appear to be about 5 per cent too low, and they may be as much as 10 or 12 per cent too low.

Pettenkofer's method is inclined to give still lower results, and although those obtained seemed to be only from 1 to 2 per cent lower than those obtained with Trillich's method, yet it appears somewhat unreliable, and one in which, under some conditions, extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 153).

In order to determine whether the presence of nitrous acid in the nitration mixtures tends to diminish the stability we proceeded as follows:—

Two nitrations were carried out with the same nitration mixture; one containing a certain quantity of nitrous acid, and the other without any. The two nitrations were started simultaneously, and the two products of nitration to be compared received exactly similar treatment as regards washing, drying, and application of the stability test. The great sensitiveness of the latter, and the numerous factors which influence it, have made this method of work necessary. The attempt was first made to carry out only one nitration with the nitration mixture free from nitrous acid. The resulting gun-cotton was treated according to the prescribed manner, and the stability then determined. We hoped to obtain comparable results from products arising from exactly similar treatment and containing various amounts of nitrous acid. But this did not prove to be the case; the results thus obtained were often quite contradictory. Hence, these experiments are here passed over, and we pass on to those conducted at the same time, according to the method above mentioned.

Experiment 1.—Two nitrations were undertaken at the same time and under exactly similar conditions, and with the mixture usual in trade of three parts concentrated sulphuric acid and one part nitric acid 1.52; one operation without addition of nitrous acid, the other with addition of 4.93 per cent N₂O₄, determined by titration with N/2 potassium permanganate. In the latter case, according to the reaction N₂O₄ + H₂SO₄ = SO₂NH + HNO₃, a certain amount of nitric acid is introduced into the nitration mixture through the nitrous acid present. An exactly equal quantity of pure nitric acid was therefore

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

Abel Test.

Day of the experiment.	Without nitrous acid.		With nitrous acid.		Check experiment.
	<i>a</i> ₁ .	<i>a</i> ₂ .	<i>b</i> ₁ .	<i>b</i> ₂ .	
5/12/1899	25' E.P.=188.5° <i>t</i> =5' 11"	27'	37' E.P.=188° <i>t</i> =5' 10"	36'	14' E.P.=195° <i>t</i> =6'
12/1/1900	44'	45' E.P.=187° <i>t</i> =5' 35"	52'	50' E.P.=186° <i>t</i> =5' 33"	13' E.P.=201° <i>t</i> =4' 30"
6/3/1900	55' E.P.=187° <i>t</i> =5' 30"	54'	64' E.P.=186.5° <i>t</i> =5' 29"	64'	15' E.P.=196° <i>t</i> =6'

The first numbers indicate the time that elapses before the reaction sets in.

E.P. = explosion-point.

t = time of heating till explosion occurs.

Temperature of water-bath = 80°.

added to the mixture containing no N_2O_4 , in order to establish similar conditions, as far as possible, in both experiments. The nitration products were then submitted to exactly similar treatment, and, after pressing out the acids and repeated washing with cold water, were cut up as finely as possible with scissors, boiled for four days in large porcelain dishes with frequent renewal of the water, then well pressed between blotting-paper, and finally placed in a vacuum desiccator for about six days until completely dry. The substances must be as dry as possible for carrying out the stability test, as the presence of a very small amount of moisture may considerably retard the beginning of the reaction. In order to check the unchanged sensitiveness of the test-paper, a sample of known stability was tested with each determination. The material used for this purpose was kept in a moist condition in a closed flask.

Together with the stability test, the explosion temperature of the product was generally determined by heating 0.01 grm. in a little glass placed in an oil-bath. The explosion temperature is dependent on the duration of the heating, to which it is inversely proportional.

At the termination of the stability test, the products were spread out on lunette glasses and allowed to lie exposed to the air, but protected from dust. From time to time their stability was again tested; once to determine the effect of long standing, and afterwards to confirm the results with a large number of determinations.

Two samples of each product, of 1.2 grms. each, were always tested simultaneously. All the determinations were carried out together and in the same apparatus.

Thomas's test.	Number of days.
<i>a</i> ₁	2½
<i>b</i> ₁	3
<i>c</i>	2

In this experiment, therefore, a diminution of stability owing to the presence of nitrous acid in nitrating cannot be proved. The gun-cotton produced by nitrating in the presence of nitrous acid even showed more favourable stability results, which must certainly not be attributed to the action of the nitrous acid, but must be mentioned as a fact. The explosion of this product occurred one to two seconds earlier, and the temperature was $\frac{1}{2}$ –1° lower than in the case of the gun-cotton produced from the nitration mixture containing no nitrous acid. But this difference is so slight that no real importance attaches to it. The explosion-points of the one product, *a* and *b*, were determined simultaneously in the same oil-bath; hence, the manner and speed of heating was the same for both, and accordingly the results may be directly compared with one another. The two explosions always followed each other quickly, often with a scarcely measurable time difference. It is remarkable that the explosion-point of *c* lies about 10° higher than that of products *a*

and *b*. It follows that the beginning of the decomposition (stability test) and the setting in of a sudden and complete decomposition (explosion-point) do not stand in a simple relation to one another.

(To be continued).

THE ANALYSIS OF WHITE-METAL ALLOYS.

By FRED. IBBOTSON and HARRY BREARLEY.

Introduction.

It has been said again and again, and it is unquestionably true, that the analyst is better equipped with processes for the analysis of iron and iron alloys than he is with means of examining any other complex metallurgical compounds. This is particularly true in relation to the analysis of alloys of white-metal, such as are used for anti-friction purposes and better class type-metals.

Close attention to and some experience with nearly every scheme which has been proposed for analysing anti-friction metals leads us to conclude that:—

- (1). While there are many processes which yield amounts of tin, antimony, lead, copper, bismuth, arsenic, &c., that total up to about 100 per cent, there are very few which give satisfactory results for the individual metals when applied to known amounts of them dissolved up altogether; and
- (2). That some means of estimating the elements singly without any preliminary separations, or merely incidental ones, as is so common in the everyday analysis of iron compounds, would be a great advantage when only partial analysis were needed, and would also be most desirable checks on the results of a general analysis.

In the following series of papers we propose, as opportunity is afforded us, to show how an estimation of a number of specific elements may be made singly; and then to describe a process for the general analysis of white-metal alloys which has yielded excellent results with mixtures of known composition in a comparatively short time.

I. The Estimation of Tin.

The titration of a hydrochloric acid solution of stannous chloride with iodine has been several times recommended as an easy and accurate means of estimating tin. The reduction of stannic to stannous chloride is generally accomplished by metallic iron, since ferrous salts do not at all interfere with the subsequent titration; this makes the process a particularly desirable one for the assay of tinned-plate.

Whether the measured oxidation of stannous to stannic salts is made in acid or alkaline solution, the avidity with which the former, particularly when hot, absorb oxygen

from the air or from water used for dilution must be guarded against. Any error is reduced to a minimum by cooling the reduced solution in an atmosphere of CO_2 , and adding nothing to it save the standard iodine and starch.

A very brief exposure of hot solutions of stannous chloride to the atmosphere is undesirable, and therefore the iron which is added in excess of that needed for the reduction of the tin must be completely dissolved. When antimony is also present, it is reduced by the iron to the metallic state, and as it is quite insoluble in hydrochloric acid no amount of boiling enables these metallic flocks to be got rid of. If the solution be carefully cooled in an inert atmosphere, and the antimony be filtered off, it is necessary only to again reduce the filtrate with iron and titrate the tin, but if the hot solution be filtered a portion of the antimony goes into solution and is again precipitated by the iron.

The antimony found in the filtrate when hot solutions of stannous chloride containing that metal are filtered, is due to the formation of stannic chloride by the oxygen of the atmosphere, and a further reduction of the same by metallic antimony. When filtered cold, not nearly so much stannic chloride can be formed, and, moreover, *cold acid solutions of stannic chloride are not reduced by metallic antimony.*

From the above, it follows that a solution containing tin and antimony may be reduced with iron, cooled in an inert atmosphere, and titrated with iodine without troubling at all about the precipitated Sb. So little is the precipitated antimony affected by the cold stannic chloride that, after the titration of the tin, it may be filtered off and estimated with very tolerable results in any of the usual ways. The following analyses are presented in support of these conclusions:—

Grm. taken.		Grm. found.	
Tin.	Antimony.	Tin.	Antimony.
0.2000	0.0400	0.2000	—
0.1200	0.1000	0.1204	0.0972
0.1000	0.1200	0.1003	0.1152
0.0400	0.2000	0.0401	—

The accurate estimation of tin in the presence of antimony is the point we are insisting upon; the simultaneous estimation of antimony is but incidental, and must in practice always give results somewhat low, particularly when the tin is very large in comparison with the antimony.

Antimony which has been precipitated with iron from its chloride solution does *very slowly* reduce stannic chloride in cold solutions, and therefore the starch blue in the above series of titrations is not quite permanent. But smelted antimony which has been ground in an agate mortar has a scarcely perceptible reducing action on cold stannic chloride, although at boiling-point it very quickly reduces it to stannous chloride. To a hydrochloric acid solution of stannic chloride there was added a few decigrams. of powdered antimony. The solution was boiled, cooled in CO_2 , and titrated with iodine. One-tenth of a c.c. of N/10 iodine was added in excess in order to form a very decided blue colour. After standing for fifteen minutes the colour had not gone. It did not disappear on heating until 60°C . was reached; and, at that temperature, it disappears very lazily on reforming with a drop of iodine.

The following test analyses show that the tin is completely reduced to stannous chloride by the antimony:—

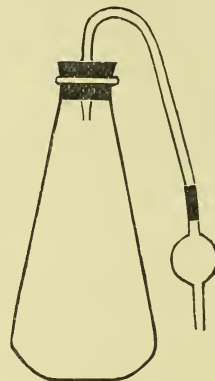
Tin added.	C.c. N/10 I used.	Tin found.
0.1750	29.7	0.1752
0.1000	16.9	0.0997
0.0480	8.3	0.0490
0.0200	3.4	0.0201
0.0080	1.4	0.0083

The reduction of stannic chloride with antimony instead of with iron or zinc, or any other metal, is obviously an improvement in so far as any excess added need neither

be destroyed in the solution nor otherwise removed. In a measure, too, the excess of antimony acts as a safeguard during the cooling of the SnCl_2 , in that any accidental oxidation while the solution is still hot is corrected. As the solution cools, the antimony becomes less able to correct such a mishap; which then, however, is less likely to occur.

The Estimation of Tin in the presence of other Elements.

In minerals and alloys tin is found associated with Fe, Mn, Al, Cr, Pb, Bi, Zn, Ni, Co, Hg, Si, Ag, Cu, S, P, As, W, and Mo, and in the course of analysis there accumulate very variable quantities of hydrochloric acid. It is desirable to know which of these elements must be separated before the stannic chloride may be reduced with antimony and titrated with iodine.



In each test 0.15 gm. of tin was used. The reduction was made in the arrangement shown in the figure, and cooled out of contact with air by dipping the tip of the bent tube into an emulsion of NaHCO_3 with freshly boiled water. By nipping the rubber connection at the right moment very little of the emulsion is needed to generate the required amount of CO_2 , and it is desirable to use as little as possible in order to minimise the addition of dissolved oxygen.

Hydrochloric Acid.—Experiments in which the proportion of HCl (1.16 specific gravity), varied from one-tenth to one-half the volume (150 c.c.) of solution gave results varying from 99.5 to 101 per cent. It is desirable to work with solutions containing the same proportion of HCl, say one-fifth the volume of strong acid.

Iron.—Exercises no influence. When metallic iron is used to reduce the tin, and SbCl_3 is also present in solution, the appearance of metallic antimony is an indication that the tin is completely reduced. Much less iron may be used than is usual, and with greater certainty, by taking advantage of this fact.

Chromium and Nickel.—Exert no interference other than may be due to the colour of their chloride solutions, and that is not serious.

Zinc, Manganese, and Aluminium.—Do not at all interfere.

Copper.—Is reduced to cuprous chloride. If the iodine is added in brisk drops to the vigorously agitated solution, so that no local excesses of iodine are formed, the results are accurate. But the results are seriously out when local excesses of iodine are allowed; e.g., only 0.1239 gm. tin was registered instead of 0.1500 when 20 c.c. N/10 iodine was run into the solution containing 0.05 gm. copper, without shaking, and then finished as usual. A white precipitate (cuprous iodide) forms. In order to delay the formation of this precipitate, and also to assist the precaution just named, it is advisable to have a larger proportion of HCl present; say, one-third the volume of acid of 1.16 specific gravity.

Cobalt.—The results were always a trifle high, but it is

so little that one hesitates to say that cobalt exerts any influence; e.g., 0.15 to grm. Sn instead of 0.1500.

Lead.—Without influence. In very dilute acid solutions lead iodide may form; but, by titrating in very acid solutions so as to prevent this, there is no difficulty when three or four times as much lead as tin is present.

Bismuth.—The yellow colour which bismuth forms in potassium iodide solutions does not interfere much with the starch blue. There is no other interference.

Arsenic.—Seriously interferes whether present as As_2O_3 or As_2O_5 . A solution containing a decigram. of arsenic and 0.15 grm. tin, treated in the usual way, needed only a few drops N/10 iodine to form the starch-blue. The same thing happens when the tin is reduced with iron. When acid solutions of soda arsenite and stannous chloride are boiled together a black graphitic-looking precipitate, insoluble in HCl, is formed. This precipitate, which contains both arsenic and tin, explains the interference.*

Phosphorus and Sulphur.—Soda phosphate and sulphate added to the stannic chloride exert no influence.

Mercury.—Is reduced to the metallic state. In hot solutions finely-divided mercury exerts a limited reducing action on stannic chloride; it is inert in cold solutions.

Molybdenum.—The characteristic Mo_2O_3 colour forms when the solution is but moderately warm, but it is not appreciably re-oxidised by the iodine. The starch-blue is very slowly discharged; this, however, leaves no uncertainty in the mind, because the normal end-reaction is so very sharp and decisive.

Tungsten.—Lower oxides are also formed. The solution may be light blue, but the starch (dark) blue can be readily distinguished notwithstanding.

The speed at which the reduction of the tin takes place depends very much on the state of division of the antimony. We use the metal ground in an agate mortar until the particles no longer glisten. With such material the reduction is completed by one minute's boiling.

It may sometimes be desired to repeat the estimation of the tin in the same liquid by again boiling, cooling, and re-titrating. This, however, cannot be done satisfactorily with metallic antimony as reducing agent. With iron, adding a few drops of SbCl_5 to show when all the tin is reduced, one and the same solution may be reduced and titrated as often as one pleases.

The Technical Department,
University College, Sheffield.

ON THE PURIFICATION OF CÆSIUM MATERIAL.†

By H. L. WELLS.

SEVERAL years ago (*Amer. Journ. Sci.*, [3], xlv., 186), I recommended the use of the yellow salt $2\text{CsCl} \cdot \text{PbCl}_4$ as a means of precipitating cæsium from its solutions. Subsequent experience has shown that the method is very convenient for removing small quantities of the rare metal from all sorts of solutions; particularly from those from which the greater part of it has been precipitated by other means. For large quantities of cæsium, however, the lead tetrachloride method, used alone, is inconvenient on account of the large amount of chloride that must be used, and because it is possible to obtain only very dilute solutions of lead chloride or of the white double salt, $\text{CsCl} \cdot 2\text{PbCl}_2$ (*Amer. Journ. Sci.*, [3], xlv., 121).

I have used extensively the salt just mentioned as a means of precipitating cæsium from concentrated solutions of the crude extract of pullcite, made by means of hydrochloric acid. The precipitation is made by adding a hot concentrated solution of the calculated amount of lead

nitrate. The precipitate is crystalline, and can be readily washed with dilute hydrochloric acid; then it can be very easily decomposed by boiling with ammonium carbonate solution. The method is satisfactory in a case where very little potassium and practically no rubidium are present, for, although it does not give a good separation from these metals, the precipitation of cæsium is nearly complete. The precipitate $\text{CsCl} \cdot 2\text{PbCl}_2$, however, is very heavy compared with the amount of cæsium that it contains, and its decomposition with ammonium carbonate produces four molecules of ammonium chloride for one of cæsium chloride. For these reasons the method has been abandoned in this laboratory in favour of the method of Godeffroy.

In precipitating cæsium according to Godeffroy's method I am accustomed to use less concentrated hydrochloric acid solutions than those that have been recommended. About one-third or one-half of the total volume of concentrated hydrochloric acid answers very well, and a solution of this kind possesses the advantage that it can be filtered by means of paper. To such a solution antimony trichloride, also dissolved in hydrochloric acid, is added as long as a precipitate forms. The latter is collected, best on a Büchner filter, and well washed with cold dilute hydrochloric acid.

To the filtrate and washings from the antimony salt, without concentrating them, lead nitrate is added at the rate of 2 or 3 grms. per litre. This salt should be dissolved in water before it is added. Chlorine gas is then passed in until the solution is saturated with it. After standing for a few hours the liquid is decanted from the precipitate of the salt Cs_2PbCl_6 (which is usually coloured green from the presence in it of the dark blue salt Cs_2SbCl_6),* and is tested by the addition of a little more lead nitrate, and chlorine also if necessary. This precipitation is so complete, as far as cæsium is concerned, that the liquid may be finally discarded. A litre of such a liquid will probably hold in solution only about 0.1 grm. of the salt Cs_2PbCl_6 , but the rubidium salt is nearly one hundred times more soluble. The lead tetrachloride salt should be washed on a Büchner funnel with cold dilute hydrochloric acid.

Formerly I was accustomed to decompose the antimony salt, $3\text{CsCl} \cdot 2\text{SbCl}_3$,† by suspending it in water, and passing in hydrogen sulphide gas; but for large quantities this is a very slow and laborious operation, and it is much more convenient to treat it in a large porcelain dish with boiling dilute ammonium hydroxide. The antimonious oxide thus produced is dense and easy to filter and wash; moreover, it may be readily dissolved in hydrochloric acid, and used again for precipitating cæsium. A little antimony goes into solution in the ammonia, but this is readily removed, best after the liquid has become slightly acid by evaporation, by passing in hydrogen sulphide, and filtering.

The removal of ammonium chloride on a large scale by ignition is a very slow operation. It is therefore best, in most cases, after the hydrogen sulphide has been removed by evaporation, to add to the concentrated solution of cæsium and ammonium chlorides, in a large porcelain dish, a liberal amount of concentrated nitric acid, and to heat cautiously until frothing has ceased. When further additions of strong nitric acid produce no change of colour nor evolution of gas upon heating, the ammonium salts are entirely destroyed, and the cæsium chloride changed to nitrate.‡ The solution of cæsium nitrate in nitric acid is then evaporated to dryness, and the residue is heated until the acid nitrate§ is decomposed, and the normal

* Concerning this compound see *American Chemical Journal*, vol. xxvi., p. 268.

† The composition of this compound was very incorrectly determined by Godeffroy, who gave it the formula $6\text{CsCl} \cdot \text{SbCl}_3$. Setterberg first arrived at the correct formula, which was afterwards confirmed by Remsen and Saunders, and also by Muthmann, and by Wells and Foote.

‡ This method of destroying ammonium chloride is due to J. Lawrence Smith. See *Amer. Journ. Sci.*, [2], xxxiv., 367.

§ A description of the acid cæsium nitrates will soon be published from this laboratory.

* Some means of eliminating the arsenic will be noticed when the general analysis of the alloys is being dealt with.

† Contribution from the Sheffield Laboratory of Yale University. From the *American Chemical Journal*, xxvi., No. 3.

373

nitrate is more or less completely fused. The evaporation of the nitrate to dryness in the presence of nitric acid over a free flame in a dish is not a difficult operation, since decrepitation takes place to a much less extent than is the case when the chloride is evaporated in the same way. A large mass of fused caesium nitrate should not be allowed to solidify quietly in the bottom of a porcelain dish, for on cooling it is liable to break the dish by its contraction. If it is stirred as it solidifies this danger is avoided.

Caesium nitrate is one of the most beautiful of salts for re-crystallisation. Like potassium nitrate, it is much more soluble in hot water than in cold, and it crystallises upon slowly cooling a hot concentrated solution in the form of large, colourless prisms. I have found that re-crystallising this salt tends to purify it from traces of rubidium, for a large quantity of the salt which showed no rubidium spectrum, upon systematic re-crystallisation, showed a distinct spectrum for that metal in the final mother-liquor. This, however, is a slow method of purification if it is desired to carry the latter to the last degree, but the nitrate obtained by one or two re-crystallisations is pure enough for any ordinary purpose, unless the original antimony salt was contaminated to an unusual extent.

The nitrate is readily converted into carbonate by mixing it with two parts of pure oxalic acid, adding a little water, evaporating to dryness, and fusing the residue in a platinum crucible. (Method of J. Lawrence Smith, *loc. cit.*).

Where the highest degree of purity in a caesium salt is desired, the salt CsCl_2I (*Amer. Journ. Sci.*, [3], xlvii., 17), by its re-crystallisation, probably offers one of the best means for accomplishing that object. It is very much less soluble than the corresponding rubidium, potassium, sodium, and lithium salts. I have found that this salt may be made very conveniently from the nitrate by dissolving one part of the latter together with one atomic proportion of iodine in about ten parts of 1:1 hydrochloric acid at a temperature just below boiling. The solution takes place quickly, and, upon cooling, the beautiful yellow salt crystallises out. It is re-crystallised by solution in hot 1:1 hydrochloric acid and cooling. One or two re-crystallisations, when each crop is well drained and washed with a little cold dilute hydrochloric acid, give, even from impure materials, a remarkably fine product. From this trihalide by ignition, best at a very gentle heat so that the mass does not fuse, pure caesium chloride may be prepared.

NOTES ON

LEAD AND CADMIUM FERROCYANIDES.*

By EDMUND H. MILLER and HENRY FISHER.

Lead Ferrocyanide.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is invariably $\text{Pb}_2\text{Fe}(\text{CN})_6$, or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows:—Lead acetate was dissolved in water and heated to boiling; to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases, as is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide, as indicated by hydrogen sulphide or by ferric chloride. They were then dried at 105°C . to constant weight. The method of analysis was in all cases as follows:—About 1 grm. was dissolved in dilute nitric acid in a casserole, and after the

addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken up with 1 per cent sulphuric acid, to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent sulphuric acid containing alcohol, filtered, and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as Fe_2O_3 . The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilised, and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess settles rapidly. The analytical results are:—

	I.	II.	III.	Average.
Lead	66.03	66.15	66.09	66.09
$\text{Fe}(\text{CN})_6$..	34.07	33.98	33.85	33.97
Potassium ..	0.50	0.48	0.45	0.47
				100.53

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis:—

	I.	II.	III.	Average.
Lead	66.26	66.06	65.98	66.10
$\text{Fe}(\text{CN})_6$..	33.54	33.77	33.90	33.70
Potassium ..	0.62	0.55	0.58	0.58
				100.38

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis, the following results were obtained:—

	I.	II.	III.	Average.
Lead	64.42	64.55	64.62	64.53
$\text{Fe}(\text{CN})_6$..	35.48	35.33	35.37	35.39
Potassium ..	0.84	0.81	0.80	0.82
				100.74

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

	I.	II.	III.	IV.	Average.
Lead	64.43	64.28	64.38	64.58	64.42
$\text{Fe}(\text{CN})_6$..	35.47	35.62	35.69	35.60	35.59
Potassium ..	0.82	0.76	0.86	0.79	0.81
					100.82

E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are:—

	I.	II.	Average.
Lead	63.73	64.02	63.87
$\text{Fe}(\text{CN})_6$..	35.51	35.02	35.26
Potassium ..	0.76	0.96	0.86

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions, and consequently, when calculated from the ratio of $\text{Fe} : \text{K} : \text{Pb}$, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess; precipitated hot as usual.

	I.	II.	Average.
Lead	63.02	63.39	63.21
$\text{Fe}(\text{CN})_6$..	34.74	34.48	34.61
Potassium ..	2.24	2.12	2.18

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that, on drying, the precipitates become either bluish or greenish in colour, due to a slight decomposition, so that the percentages of $\text{Fe}(\text{CN})_6$, which are calculated from the iron, are high (for the $\text{CN} : \text{Fe}$ ratio is higher in $\text{Fe}(\text{CN})_6$ than in $\text{Fe}_7(\text{CN})_{18}$ or $\text{Fe}_5(\text{CN})_{12}$).

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxii., No. 9.

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same, the composition is the same whether ferrocyanide or lead is in excess.

Berzelius (*Ann. Chem. Phys.*, 1820, xv., 157) states that, when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is $\text{Pb}_2\text{Fe}(\text{CN})_6$. Using the most recent atomic weights, this corresponds to a percentage composition of—

Lead	66.10
$\text{Fe}(\text{CN})_6$	33.97

Our results are, with lead in excess :—

Lead	66.09
$\text{Fe}(\text{CN})_6$	33.97

With ferrocyanide in excess :—

Lead	66.10
$\text{Fe}(\text{CN})_6$	33.70

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac (*Gmelin's Handbook of Chemistry*, London, 1852, vol. vii., p. 490) that "the precipitate, for however long a time it may have been washed, retains from 6 to 9 per cent of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made:—A solution of potassium ferrocyanide was very carefully standardised against metallic zinc and freshly ignited zinc oxide. The conditions being:—Bulk, 200 c.c.; acidity, 2 c.c. concentrated hydrochloric acid; temperature, about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0.3 c.c. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 c.c. = 0.005857 gm. of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows:—

Neutral Solution.—Separate portions of metallic lead, of about 1 gm. each, were dissolved in nitric acid, hydrochloric acid added, and evaporated to complete dryness; the lead chloride was then dissolved in hot water, diluted to 200 c.c., and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0.02454 to 0.02461; average, 0.02458.

Acetic Acid Solution.—Six determinations gave from 0.02450 to 0.02458; the average coinciding with the two most satisfactory titrations is 0.02454 gm.

Hydrochloric Acid Solution.—In a solution containing one drop of concentrated hydrochloric acid, the results were from 0.02441 to 0.02446; average, 0.02444 gm. With 1 c.c. of hydrochloric acid the results were unreliable, on account of the solubility of the precipitate.

Assuming that the precipitates formed are in one case $\text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2$, and in the other $\text{Pb}_2\text{Fe}(\text{CN})_6$, or that an amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4.278. This gives by calculation from the zinc standard, 0.0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimetre in no case reach this value, and although the variations are not so great as is shown from the analyses of the precipitates, they are in exactly the same order, and so confirm the statement that increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's statement (*Journ. Amer. Chem. Soc.*, 1893, xv., 550), that a solution containing 10 grms. per litre of crystallised potassium

ferrocyanide will equal 10 milligrms. of lead per cubic centimetre, and are at complete variance with a statement by Furman (*"Manual of Practical Assaying,"* p. 139) that it requires 16 grms. per litre for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

Cadmium Ferrocyanide.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0.3 to 0.4 gm. each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 c.c. of hot water, and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator, as is the case with manganese, so that the end tests in these titrations were made on filter-paper, placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0.0071 and 0.00727 gm. of cadmium per cubic centimetre.

In a solution containing 1 c.c. of 50 per cent acetic acid the results ran from 0.00699 to 0.00702 gm. of cadmium; average, 0.0070 gm.

In a solution containing 1 to 2 c.c. of concentrated hydrochloric acid, the average of six determinations on cadmium oxide gave 1 c.c. = 0.007177 gm. of cadmium; this was checked by four tests with metallic cadmium, which gave 0.007165 gm., or a general average of 0.00717 gm. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain, but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent solution of copper sulphate, as recommended by Moldenhauer for zinc (*Chem. Zeit.*, 1889, xiii., 1220, and 1891, xv., 223). The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0.9 c.c. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 c.c.:—0.00669, 0.00678, 0.00674, 0.00674; average, 0.00674 gm. of cadmium per cubic centimetre.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann (*Ann. Chem. u. Pharm.*, 1868, cxlv., 235), $\text{CdK}_2\text{Fe}(\text{CN})_6$; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is $3\text{Zn} = 2\text{Cd}$, and the strength of the ferrocyanide solution used would be 1 c.c. = 0.00671 gm. cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulæ have been given for cadmium ferrocyanide. Dammer gives it the normal composition $\text{Cd}_2\text{Fe}(\text{CN})_6$, and cites Wittstein (*Büchner's Repertorium der Pharm.*, lxiii., 316—317) as his authority, but the original article gives neither formula nor analysis.

Wyrouboff (*Ann. Chim. Phys.*, 1878, [5], viii., 449) gives the composition under all conditions as $\text{K}_5\text{Cd}_5(\text{Fe}(\text{CN})_6)_4$, which has been altered in Comey's "Dictionary," so as to satisfy the valence of the $\text{Fe}(\text{CN})_6$ radical to $\text{K}_6\text{Cd}_5(\text{Fe}(\text{CN})_6)_4$. Assuming that this is the precipitate formed, the ratio as regards ferrocyanide becomes $6\text{Zn} = 5\text{Cd}$, and the strength of the solution used would be 1 c.c. = 0.00838 gm. cadmium.

Our results in acid solutions are intermediate between these values, and indicate a variation in the composition of the precipitate between the formulæ of Hermann and of Wyrouboff. They are confirmed by a statement by Mackay (*Journ. Amer. Chem. Soc.*, 1899, xxi., 940) that it requires about 2½ per cent less potassium ferrocyanide to precipitate cadmium than is required by the formula

$\text{CdK}_2\text{Fe}(\text{CN})_6$, or, in other words, the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that $2\text{Zn} = 2\text{Cd}$.

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started, and while no results have yet been obtained, the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

EAST LONDON TECHNICAL COLLEGE.

A Course of 12 Lectures, with Laboratory Instruction, on ELECTRO-CHEMISTRY will be given by Prof. R. A. LEHFELDT, D.Sc., on Friday Evenings, commencing on October 11th. Lecture, 7-8; Laboratory, 8-10. The Course will deal with the GENERAL THEORY OF ELECTRO-CHEMISTRY and its chief Industrial Applications. Fee, 10s. Particulars on application.

RESEARCH FELLOWSHIP IN CHEMISTRY.

THE RESEARCH FELLOWSHIP founded by the LEATHERSELLERS' COMPANY for the encouragement of Higher Research in Chemistry in its relation to Manufactures, tenable at the City and Guilds Central Technical College, being vacant, the Executive Committee of the City and Guilds of London Institute is prepared to consider applications. The Grant made by the Company to the Institute for this purpose is £150 a year. Copies of the scheme under which the Fellowship will be awarded may be had from the HONORARY SECRETARY of the Institute, Gresham College, 91, Basinghall Street, E.C.

CITY OF LONDON COLLEGE, WHITE STREET, MOORFIELDS, E.C.

MICHAELMAS TERM commences SEPTEMBER 30th.

EVENING CLASSES in CHEMISTRY, BOTANY, GEOLOGY, BIOLOGY, and all Science subjects. Well equipped Laboratories for Practical work. Low fees. Prospectus gratis on application to—
DAVID SAVAGE, Secretary.

INSTRUCTION IN PURE CULTIVATION OF YEAST, According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactures, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered, at 2s. 6d. per volume.

6 & 7, CREED LANE, LUDGATE HILL, E.C.

ACETATE OF LIME, BROWN, 67-68 %.

WOOD NAPHTHA. METHYL ALCOHOL.

Manufactured by
STORA KOPPARBERGS BERGSLAGS AKTIEBOLAG,
FALUN (SWEDEN).

MACMILLAN & CO.'S BOOKS FOR CHEMICAL STUDENTS.

Second Edition Now Ready.

INTRODUCTION TO PHYSICAL CHEMISTRY.

By JAMES WALKER, D.Sc., Ph.D.,
Professor of Chemistry in University College, Dundee.

8vo, 10s. net.

JOURNAL OF EDUCATION:—"The author has succeeded admirably in his task, and the work should be gratefully received by those for whom it is intended."

PRACTICAL ORGANIC CHEMISTRY for ADVANCED STUDENTS.

By JULIUS B. COHEN, Ph.D.

Globe 8vo, 3s. 6d.

NATURE:—"The best elementary book, in the English language, on practical organic chemistry."

Second Edition Now Ready.

THE SCIENTIFIC FOUNDATIONS of ANALYTICAL CHEMISTRY Treated in an Elementary Manner.

By Professor WILHELM OSTWALD, Ph.D. Translated with the Author's sanction by GEORGE M'GOWAN, Ph.D.

Extra crown 8vo, 6s. net.

CHEMICAL NEWS:—"We can strongly recommend the book both to advanced chemists and to analytical students."

Third Edition Now Ready.

BLOWPIPE ANALYSIS. By J. LANDAUER. Authorised English Edition by JAMES TAYLOR, B.Sc., Wh.Sc., A.R.S.M. Globe 8vo, 4s. 6d.

CHEMICAL LECTURE EXPERIMENTS. By FRANCIS GANO BENEDICT, Ph.D. Crown 8vo, 8s. 6d. net.

ELEMENTARY PHYSICS AND CHEMISTRY. In Three Stages. By Prof. R. A. GREGORY, F.R.S., and A. T. SIMMONS, B.Sc. (Lond.) Globe 8vo, 1s. 6d. each.

A PRIMER OF CHEMISTRY. By Sir HENRY E. ROSCOE, F.R.S. Illustrated. With Questions. Pott 8vo, 1s.

CHEMISTRY FOR ORGANISED SCHOOLS OF SCIENCE. By S. PARRISH, B.Sc. A.R.C.S. (Lond.) With Introduction by Dr. FORSYTH. Globe 8vo, 2s. 6d.

INORGANIC CHEMISTRY FOR ADVANCED STUDENTS. By Sir HENRY ROSCOE, F.R.S., D.C.L., LL.D., and ARTHUR HARDEN, Ph.D. M.Sc. (Vict.). With Fifty-four Illustrations in the Text. Globe 8vo, 4s. 6d.

A TREATISE ON CHEMISTRY. By H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S.

New Edition completely revised by Sir H. E. ROSCOE, assisted

by Drs. H. G. COLMAN and A. HARDEN.

VOLUME I.—THE NON-METALLIC ELEMENTS. 8vo., 21s.

VOLUME II.—THE METALS. 8vo., 31s. 6d.

* * The two volumes as they now stand form the only complete work, up to date, on Inorganic Chemistry in the English language.

VOL. III. Organic Chemistry. Parts I., II., IV., and VI., 21s. each.

Parts III. and V. 18s. each.

INORGANIC CHEMISTRY FOR BEGINNERS. By Sir HENRY ROSCOE, F.R.S. Assisted by JOSEPH LUNT, B.Sc. Globe 8vo, 2s. 6d.

LESSONS IN ELEMENTARY CHEMISTRY, INORGANIC AND ORGANIC. By Sir H. E. Roscoe, F.R.S. Sixth Edition, thoroughly revised, 4s. 6d.

A JUNIOR COURSE OF PRACTICAL CHEMISTRY. By FRANCIS JONES, F.R.S.E., F.C.S., Chemical Master in the Grammar School, Manchester. With a Preface by Sir H. E. Roscoe, F.R.S. (Eighth Edition). Globe 8vo, 2s. 6d.

AN INTRODUCTION TO THE STUDY OF CHEMISTRY. By W. H. PERKIN, Jr., Ph.D., F.R.S., Professor of Organic Chemistry in the Owens College, Manchester, and BEVAN LEAN, D.Sc., B.A. (Lond.). Globe 8vo, 2s. 6d.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2185.

ON THE DETECTION AND ESTIMATION OF ARSENIC IN BEER AND ARTICLES OF FOOD.*

By WILLIAM THOMSON, F.R.S.Ed., F.I.C., &c.

TOWARDS the end of last year it was discovered that a danger which was recognised as a possibility had become a reality, viz., that sulphuric acid containing large quantities of arsenic trioxide had been employed for the conversion of starch into sugar, and that such contaminated sugar had been employed in the brewing of beer, with the result that thousands of people in Manchester and the neighbourhood had suffered from more or less acute arsenical poisoning. This calamity led to the examination of beer and the materials employed in its manufacture, and it was for the first time discovered that arsenic must have been during the last century almost always contained in beer in more or less appreciable or poisonous quantities.

Arsenic is present in nearly all malts and hops, and it is introduced by the process of drying which is nearly universally employed. This process consists in placing the sprouted barley (malt) on the floor of a room covered with perforated tiles or wire-cloth, and making a large fire in the room underneath with coke or anthracite coal; these fuels contain arsenic in greater or less quantity, which volatilises as arsenic trioxide, and condenses on the malt. Coke, however, usually contains a much larger quantity than anthracite.

A disease amongst beer drinkers has long been recognised in Manchester and the district (where coke is employed largely for drying malt), as peripheral neuritis, and from its supposed connection with the consumption of beer it has been called also alcoholic neuritis.

It is curious, however, that in Scotland, where presumably as much, if not more, alcohol per head is consumed than in Lancashire, alcoholic or peripheral neuritis amongst whiskey drinkers is almost unknown. This has led to the suggestion that the so-called alcoholic neuritis is really arsenical neuritis.

It has also been shown that arsenic administered along with alcohol is a much more potent poison than when given in the ordinary way medicinally. Under these conditions it becomes exceedingly important that some reliable method should be found for detecting and estimating minute quantities of arsenic in beer or in food.

It has been suggested that large quantities of materials, such as beer, should be treated with sulphuretted hydrogen, and the arsenic separated and determined by direct weighing. This, however, involves a large amount of work, and the results cannot be regarded as satisfactory when determining such minute quantities as, say, the $\frac{1}{1000}$ th of a grain to the gallon. I have therefore been led to make experiments with a view of finding, if possible, a process which should be simple and reliable for detecting and estimating minute quantities of arsenic when contained in beer and food stuffs. After a large number of experiments I found that the most satisfactory method was to destroy all the organic matter contained in the beer or any article of food by means of nitric acid together with small quantities of sulphuric acid, and after the whole of the nitric acid had been removed by evaporation, to dilute the resulting liquid to a standard volume, and take if necessary an aliquot part of the solution for treat-

ment in the Marsh apparatus, so as to obtain as nearly as possible a mirror of minimum standard intensity on the heated tube through which the hydrogen is passed. By this means very reliable approximate estimations of the quantities of arsenic up to the $\frac{1}{1000}$ th of a grain per gallon of beer or per pound of food may be made when other conditions are fulfilled, and when working on 50 c.c. of liquid or on 5 grms. of solid, the chief of which is that sulphuric acid freed from arsenic by distilling with chromic acid should be employed along with zinc, which is practically chemically pure, and which is not readily acted upon by dilute sulphuric acid, a drop of a pure solution of sulphate of copper being required to start the reaction.

Zinc which is readily acted upon by sulphuric acid, and which gives off gas freely, usually retains some of the arsenic; so that whilst a blank test shows freedom of the zinc from arsenic, it also shows freedom from arsenic when a very minute quantity of that metal is added to the contents of the apparatus.

I have found that mercury in contact with zinc in the Marsh apparatus holds back the whole of any minute quantity of arsenic; magnesium, tin, and lead hold back a large proportion of any minute quantity; whilst aluminium and copper hold back small proportions of minute quantities of arsenic. When the total quantity present in the Marsh flask approaches $\frac{1}{1000}$ th of a grain, the deposit is liable to take place in two rings of the metal with a space free from any deposit between them. The first ring nearer the flame is crystalline metallic arsenic and of a metallic brown colour; the second ring is of a bluish colour, and is evidently an allotropic modification occurring as fine dust or in flakes. I have prepared considerable quantities of these deposits, and taken their specific gravities. The first has a specific gravity of 5.705, and the second a specific gravity of 4.769. The formation of this allotropic modification as a second ring deposit is extremely inconvenient when estimating minute quantities, as it increases the difficulty of comparing the mirrors obtained, with standard mirrors, and I have spent much time in trying to understand why arsenic should be deposited in this curious manner in two broad rings of different colours, with a space of an eighth to a quarter of an inch quite free from arsenic between them. It naturally occurs to one to ask, what is the law which makes a deposit from a continuous stream of hydrogen containing minute quantities of arseniuretted hydrogen of one form of arsenic behind the heated part of the tube, then that the arsenic liberated by the heat should jump over a considerable space, which is left clear and free from deposit, and, finally, that it should deposit as arsenic of a different colour, and presumably different molecular constitution, in another and separate ring further on? These deposits do not take place in very distinct rings when the hydrogen is saturated with moisture. The separate deposits are most marked when the hydrogen is passed through a single drying tube of chloride of calcium, and it again ceases to be very marked when the hydrogen is excessively dried by passing over strong sulphuric acid and the chlorides of zinc or calcium or other strongly hygroscopic substance; the deposits when the gas is supersaturated with water, or when extremely dry, being distributed slightly and evenly along the tube behind the first brown mirror.

I have ascertained that these second arsenic mirrors are entirely prevented by the presence of a small quantity of the vapours of such bodies as ether, alcohol, petroleum spirit, benzene, or acetic acid, and the arsenic deposited under these conditions is of precisely the same bright metallic brown colour. As these deposits presumably differ from each other by their molecular constitution only, one would expect that the action of these vapours (which do not produce any deposit when they are passed along with hydrogen free from arsenic through glass tubes heated to redness), is also of a purely molecular nature. This bluish coloured arsenic, which exists as a fine powder, when gently heated by a Bunsen flame loses

* Read before the British Association (Section B), Glasgow Meeting, 1901.

its blue colour, and becomes crystalline, and appears to be converted into the first or brown form.

It is an important question which may possibly be settled by the Royal Commission at present holding its inquiry, as to what quantity of arsenic should be allowed to be present in beer; some allege that everything contains arsenic, and one has only to extract from a sufficiently large quantity of any material to obtain evidence of its presence.

It seems to me that if evidence of appreciable quantities of arsenic can be obtained from, say, 50 c.c., *i.e.*, less than a sherry wine glassful of beer, or from 5 grms. of malt or dried food by any test whatever, that such beer or food should be condemned. I must confess that such a standard would condemn the beer from almost every brewery in the country at the present moment. It is impossible to accurately test the beer from every brewing, and as the present method of drying the malt will contaminate it with arsenic to some extent, and it may do so to a serious extent without the cognisance of the maltster. The only practicable method seems to be to insist on the practical absence of arsenic from beer or food by devising methods of drying the malt or preparing the food which will not contaminate it.

I must acknowledge my indebtedness to my assistant, Mr. W. E. Wild, B.Sc.(Vit.), who has aided me by his careful and painstaking work.

THE CLEARING OF TURBID SOLUTIONS AND THE MOVEMENT OF SMALL SUSPENDED PARTICLES BY THE INFLUENCE OF LIGHT.*

By G. QUINCKE (Heidelberg).

TURBID solutions or suspensions (*trübe Lösungen Trübungen*) I call water, in which many small solid or fluid particles are suspended for a long time. The small particles are visible with the microscope.

Colloidal solutions of doubtful character will be discussed later.

Sedimentation, or formation of flocks (flocking) is observed if small quantities of acid or salt solutions are brought in contact or mixed with the turbid solution.

For instance, the sand-bank at the mouth of a river is the effect of the clearing power of the sea-water on the particles of clay suspended in the fresh water of the river.

Turbid solutions of clay, kaolin, silica, gum-mastic are flocked by so small quantities of acid or salt that the increase of weight by the clearing substance cannot explain the augmented velocity or the flocking of the falling particles, or the sedimentation of the turbid solution.

Franz Schulze (*Poggendorff's Ann.*, 1866, cxxix., p. 366), and Schloësing (*Comptes Rendus*, 1870, lxx., p. 1345), found 1/10,000—1/100,000 of calcium or magnesium salts sufficient to clear suspensions of clay. Bodländer (*Gött. Nachr.*, 1893, p. 267) has measured the clearing or coagulating power of different salts for suspensions of kaolin; Hardy (*Proc. Roy. Soc.*, 1900, lxi., p. 111—119) for suspension of gum-mastic; Spring (*Rec. Trav. Duin. des Pays-Bas*, 1900, x., 2 Ser., 4, No. 3, pp. 294, 222) for suspensions of gum-mastic, kaolin, silica; Bodländer found suspensions of kaolin flocked, if the quantity of the added salt has been greater than a distinct, very small quantity; the "*Schwellenwerth*" of the clearing substance. Electrolytes promote, insulators retard the clearing of the suspensions (Barus, *Phys. Zeits.*, 1888, xii., p. 563; Bodländer). The clearing power of a salt depends on the valence of the salt, and the kation of the electrolyte (Hardy, Spring).

According to Hardy (*loc. cit.*), the particles of gum-mastic or heat modified proteid move contrary to an electric current.

In presence of a minute amount of barium chloride or free acid, the particles of gum-mastic or heat-modified proteid move with the electric current. At the isoelectric point, for a distinct small quantity of barium chloride or acid, the electric movement vanishes, and coagulation or precipitation occurs.

An explanation of the clearing power of the acids or salts is not given.

In the coagulated solutions I found flocks adhering to the walls of the glass vessels, and many air bubbles divided through the flocks. Both phenomena prove that on the surface of the flocks, at least a short time after formation of the flocks, an oily viscous fluid exists. On the surface of separation of this oily fluid with the surrounding aqueous fluid, a surface tension acts, and air-bubbles are separated as in the limit of two heterogeneous fluids. Probably changes of the surface tension of the boundary of oily and aqueous fluid, and the periodical spreading of heterogeneous liquid, will excite vortices, and join together the small suspended particles to form the flocks. The surface forces are the same as the forces which form foam-cells by the contact of alkaline oleates with water, which I demonstrated at the meeting of the British Association at Oxford, 1894. The flocking influence of so very small quantities of clearing matter is now intelligible.

I shall prove that this explanation is the right one.

Alcoholic solution of gum-mastic gives in a large mass of water many unseen threads and foam-walls, in which are distributed a great many small visible spheres. Copper sulphate added to the water with the mastic-foam moves the foam-walls against the copper sulphate, they become clearer, and are dissolved. The sphere and the foam-walls prove the formation of an oily viscous fluid by the action of water and gum-mastic, which I will call mastic-hydrate, and which possesses a surface tension in the surface of separation with water. The copper sulphate is soluble in water and in mastic-hydrate, has the surface tension zero in the limit with water and in the limit with mastic-hydrate, and must be spread out on the common surface of mastic-hydrate and surrounding water. The spreading excites vortices, and draws the surrounding matter towards the spreading centre, the surrounding fluid is stirred up, a new portion of copper sulphate is brought in contact with the mastic surface, spreads out, and so is repeated in short periods; the spreading of the added salt, the formation of vortices, and the mastic particles are attracted by the copper solution.

The solution of copper sulphate, which is put with a long thin funnel under a turbid solution of mastic in a test-tube, will diffuse in the mastic solution, spread out on the surface of the suspended particles, excite vortices, draw the mastic particles together or against the walls of the test-tube, where they will adhere. The connected viscous matter will flow together and form drops, bubbles, or coherent foam-cells (flocks). On the surface of the mastic-hydrate is collected, as in all new built boundaries of two heterogeneous fluids, the absorbed air in small bubbles; one part of the flocks with the adhering air will rise, the other part with the larger flocks will sink to the surface of the salt solution.

Spreading or vortices of sufficient energy and connection, or flocking of the suspended particles, demands a certain concentration of the copper sulphate, corresponding to the "*Schwellenwerth*" of Bodländer.

Solutions of NaCl, HCl, $K_2Cr_2O_7$, $FeCl_3$ spread out on the surface of mastic-hydrate as with $CuSO_4$, and have the surface tension zero. The coagulation or clearing of mastic solutions by this salt solution is explained in the same way as with $CuSO_4$.

Turbid solutions of kaolin in glass cylinders of 100×10 c.m. form a series of horizontal layers having about the same distance. After two months a great many flocks adhered on the shadow side of the glass. Under the microscope the flocks showed threads or tubes of a downward flown liquid, with spheroidal enlargements

* Read before the British Association (Section A), Glasgow Meeting, 1901.

or contractions (*Anschwellungen und Einschnürungen*). The sediment on the ground of the glass cylinder had the appearance of solidified liquid, contained deformed bubbles and coherent foam-cells, smooth spheres of 0.002—0.0004 m.m. diameter, with greater refraction than the neighbourhood.

The particles of kaolin have been covered by the influence of the water with an oily, viscous fluid, probably silica hydrate, on the surface of which another fluid has been spread out. The periodical spreading has combined the suspended kaolin particles in larger flocks, which slowly have been sunk to the ground, or were drawn by the vortices against the glass walls where the particles covered with oily fluid adhered. The oily silica hydrate has formed spheres, bubbles, or coherent foam-cells, and has been afterwards solidified.

Turbid solutions of 1/1000 kaolin give in test-tubes solutions over CuSO_4 , FeCl_3 , CaCl_2 , or $\text{Ca}(\text{HO})_2$ foam-flocks with thin walls, in which many little grains are distributed, or with thick foam-walls, in which again small chambers or cells with thin walls are enclosed. The flocks of kaolin adhered to the glass wall, so have been built in the beginning by viscous fluid.

Also over solutions of sugar, solutions of kaolin have formed two thick flock-layers.

Turbid solutions of potash soap have shown flocks over chloroform, sulphide of carbon, aqueous solution of sugar, CuSO_4 , ClH .

Turbid solution of oleic acid has been flocked by solutions of ClH , CuSO_4 , or chloroform, sulphide of carbon, and sugar. Turbid solution of China ink by solution of CuSO_4 and ClH .

The order of the flocking solution, governed by the velocity of the clearing, changes with the concentration of the suspended particles.

Electrolytes and insulators may be clearing substances.

The flocks of mastic and kaolin adhered to the shaded side of the glass wall by the artificial clearing by means of the light.

The views of Barus, Hardy, and Spring on the clearing power of different liquids, especially of the electrolytes, are not confirmed by my experiments. It is not proved that the kation of the clearing electrolyte is the clearing matter.

The flocks of gum-mastic in the turbid solution, are formed by a thin layer of mastic salt solution (*Mastixhaltiger Salzösung*), which is connected to the surface of the mastic particles by molecular force. This thin layer of mastic salt solution will develop to sensible electromotive force in contact with the pure salt solution outside, and no movement of the suspended particles with the thin layer by an electric current will be possible. My theory explains the theory of the flocks and of the isoelectric flocks of Hardy, which are not moved by the electric current. The process of clearing is the same in all turbid solutions. All flocked particles, or in suspended particles united in flocks, are covered with a thin layer of solution, nearly isoelectric with the surrounding pure salt solution, and cannot be moved by electric forces.

If by the influence of light more spreading fluid is formed on the light side than on the shaded side of the suspended particles, the suspended particle will go towards the light. I will call this phenomenon positive photodromy.

If the influence of light would stop the formation of the spreading solution, or the spreading film, the flocks would go to the shaded side, or would show negative photodromy.

A retarding influence of the light is not probable, but many physicists suppose with E. Becquerel that there is a retarding or stopping influence of red light, on the fluorescence of Sidot's blende. I think that the negative photodromy may also be explained by the heating effect of the light, and the formation of air-bubbles on the light side of the suspended particles. The air-bubbles will hinder the spreading of the newly formed solution on the surface of the suspended particles, and the vortices of sufficient energy will only exist on the shaded side; the flocks will go away from the light, or show negative photodromy.

The Stability of Turbid Solutions.

Turbid solutions of gum-mastic, silica, sodium or potassium silicate, kaolin, gummi-gutti, shellac, soap, proteid, can remain apparently unchanged for months or years, but after some weeks or months we can always find flocks on the bottom of the solution.

Moreover, horizontal layers are formed with more or less suspended particles. What is the reason of the stability of the turbid solution? Hardy and J. J. Thomson see the reason for the stability in the electromotive force on the boundary of the suspended particles and the surrounding fluid, which hinders the movement of the solid particles, while, according to Dorn, electric work is done by the displacement of the particles. The action is the same as if the viscosity of the fluid has been increased.

That electric work is done by the displacement of suspended particles, or by the displacement of fluids over the solid walls of porous bodies, and that electromotive force exists at this boundary, has been known before the researches of Dorn, and is a consequence of my old researches on capillary electric current. If the explanation of Hardy and J. J. Thomson be right, the turbid solutions must have the greatest stability, if the suspended particles show the greatest electromotive force in contact with the surrounding fluid, i.e., sulphur, silica, shellac suspended in water, but shellac gives turbid solutions of little stability. It may be that the electromotive force at the boundary of liquid and suspended particles may increase the stability of the suspension, but the principal reason of the stability may be that the velocity of the falling particles is not constant, but variable or periodic. The impulses of the periodic velocity are propagated with the velocity of sound, and will be reflected inside or at the bottom of the turbid solution. The direct impulse will interfere with the reflected impulses, and the particles will be collected in horizontal layers at distances of half a wave-length.

The air also separated at the common surface of the suspended particles and the surrounding liquid has in many cases an important influence, and will be attached to it or will cover it. The diameter of the air-bubbles or thickness of the thin air cover may be so small that it is not possible to see it with the best microscope, but it forms the condensation nuclei for former separated masses of absorbed air.

In turbid solutions of gum-mastic, soap, or oleic acid one may see these air-bubbles. In turbid solutions of kaolin or silica they act as a Cartesian diver; the suspended particles and the layers of particles rise if they are lighted up by sunshine, and sink again in the shadow by a change of density or volume of the air.

MONAZITE FROM NEW GRANADA.

By NICHOLAS J. BLUMAN.

THE following is a recent analysis of a sample of monazite from New Granada:—

Cerium oxide, Ce_2O_3	25.02
Lanthanum oxide, La_2O_3	22.41
Thorium oxide, ThO_2	18.00
Manganese oxide, MnO	1.21
Calcium oxide, CaO	2.13
Tin oxide, SnO_2	3.00
Phosphoric acid, P_2O_5	28.23
Iron	} traces
Zinc	
Sulphur	
	100.00

The specific gravity of the mineral is 6.001, hardness 5, colour reddish-brown.

ON THE INVERSE RELATION OF CHLORINE
TO RAINFALL.*

By WILLIAM ACKROYD, F.I.C.

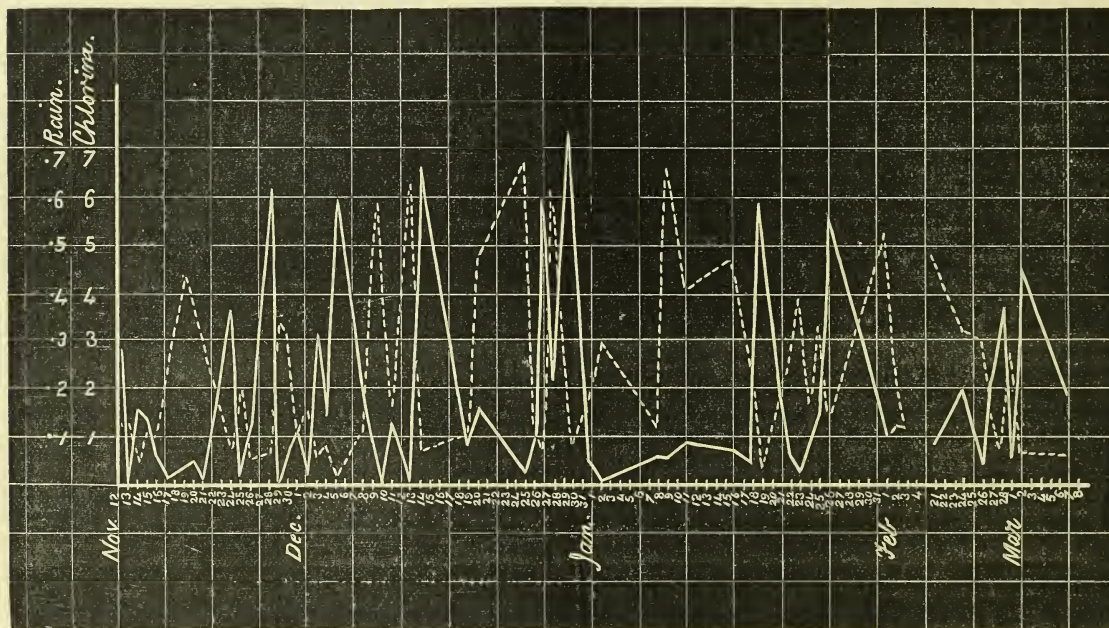
ROBINET and other French observers have shown that the early portions of a shower contain more fixed matter in solution than those subsequently collected (Smith on "Air and Rain," p. 268), from which it follows that on the same day there must exist an inverse relation between the amount of matter in solution and the quantity of rainfall.

Collecting various parts of a shower, however, is inconvenient as involving too much labour, and would, moreover, only accentuate the apparently erratic differences which exist when rainfalls of various dates are compared

ON THE
ABSORPTION OF AMMONIA FROM POLLUTED
SEA-WATER BY THE *ULVA LATTISSIMA*.*

By Prof. LETTS, D.Sc., Ph.D., and JOHN HAWTHORNE, B.A.

IN a previous research (*B.A. Report*, 1900, and *Proc. Roy. Soc. Edin.*, 1901, p. 268), it was shown that the occurrence of this sea-weed in quantity in a given locality is associated with the pollution of the sea-water by sewage, the evidence being of three kinds:—(1) The high proportion of nitrogen contained in the tissues of the *ulva*; (2) an examination of certain localities in which the sea-weed occurs in abundance, and of others from which it is virtually absent; and (3) experiments on the assimilation of nitrogenous compounds by the growing *ulva* from sea-water artificially polluted.



—— Rainfall, in tenths of an inch.
----- Chlorine, in parts per 100,000.

among themselves, for which reasons probably observers have generally been satisfied with monthly or half-yearly averages. The writer finds that when the periods of observation are shortened to daily estimations, say, of the chlorine, it clearly appears that minimum amounts of rainfall are marked by maxima of chlorine contents, and *vice versa*. Thus, in a daily comparison where the results are plotted for tenths of an inch of rainfall and parts per 100,000 of chlorine, the respective curves interlock, and each chlorine peak has its corresponding rainfall hollow. This will be seen on following the plotted observations in the diagram for Halifax, November 12th, 1900, to March 7th, 1901. It is also apparent in the diagrams for country rainfall, which illustrate my paper "On the Distribution of Chlorine in Yorkshire," Part II., and where the observations are weekly. Regarded as a method of research it will be found that marked parallelism of chlorine curves, where several are compared for the same times, and widely separated areas, may be looked upon as being due to common causes; as, for example, the atmospheric transportation of salt from the sea, or the spreading of the great smoke cloud of manufacturing centres.

Commencing these latter experiments somewhat cautiously, it was first proved that all the ammonia was removed from a sample of sea-water considered to be somewhat highly polluted (0.046 part ammonia per 100,000) by a few days' contact with the sea-weed. Next, it was found that the absorption occurred in less than twenty-four hours, while later experiments have shown that the remarkable power of assimilating ammonia which the sea-weed possesses had been altogether underestimated, as well as the rapidity with which the absorption occurs. The method of experiment was that previously employed. A sample of the polluted sea-water was first analysed and placed in a glass dish. Next a frond of the *ulva* was immersed in it, and, finally, portions of the sea-water withdrawn and again analysed after suitable intervals. Two different series of experiments were made, the first with a solution of ammonium chloride in pure sea-water, and the second with a mixture of sea-water and the effluent resulting from the treatment of sewage by the so-called "bacteria beds." All the experiments in the first series were made with the same piece of sea-weed, which had an area of about 200 square inches; and a

* Read before the British Association (Section B), Glasgow Meeting, 1901.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

similar remark applies to the second series, in which, however, several pieces of sea-weed were used, having a total area of about 600 square inches. Individual experiments in both series were made to test the absorptive power of the *ulva* in relation to concentration (of the ammonia), as well as the effects of light and darkness. The following table gives the chief results obtained;—

Absorption of Ammonia by Ulva latissima from—

Solution of Ammonium Chloride and Sea-water.
(Area of Fronds 200 square inches).
(Volume of Mixture, 2½ litres).

No. of Expt.	Parts of Ammonia per 100,000 of liquid originally present.	Percentage of Ammonia absorbed after					In
		Hours—					
		1.	2.	3.	4.	5.	
1A	0.085	59	81	91	—	—	Daylight.
5A	0.180	58	88	96	97	—	
4A	0.085	37	77	87	91	—	Darkness.
7A	0.060	29	44	56	67	75	

Mixture of Bacteria Bed Effluent and Sea-water.
(Area of Fronds 600 square inches).
(Volume of Mixture 2½ litres).

No. of Expt.	Parts of Ammonia per 100,000 of liquid originally present.	Percentage of Ammonia absorbed after					In
		1.	2.	3.	4.	5.	
1E	0.084	64	82	91	—	—	Daylight.
6E	0.412	59	86	96	98	99	
3E	0.080	18	45	58	—	—	Darkness.
4E	0.095	58	79	87	94	96	
5E	0.532	43	63	73	98	—	

The general conclusions to be drawn from the experiments are as follows:—

(1). The absorption of ammonia by the sea-weed is very rapid, and with the mixtures used practically all the ammonia was absorbed in five hours (with one exception, when 75 per cent was lost).

(2). The amount absorbed is greatest during the first hour of contact, and then rapidly falls off.

(3). Although the concentration of the ammonia exercises some effect on the proportion absorbed, it is by no means so considerable as might have been expected.

(4). The sea-weed absorbs ammonia both in daylight and in darkness, but the proportion in the latter case is rather less than in the former.

(5). The effects of an increased area of the sea-weed on the proportion of ammonia absorbed are not so great as might have been expected.

These results may be of practical importance in those districts where a serious nuisance results from the decay of large quantities of the *ulva* which have been washed ashore, or which have accumulated in shallow water. For it seems probable that by allowing the effluent from the bacterial treatment of sewage (which treatment gets rid of much of the ammonia originally present) to remain in contact with the growing *ulva* in specially constructed ponds containing sea-water, before discharging it into the sea itself, the ammonia or nitrate will be absorbed, and that the mixture of effluent and sea-water will then no longer provide nourishment for the *ulva* in the sea itself, and that, consequently, the sea-weed will be so much reduced in quantity in the district as to cease to give rise to a nuisance.

The stimulating effects of the ammonia or effluent were evident from the rapid evolution of oxygen from the surface of the sea-weed, which always occurred about fifteen minutes after the addition of the polluting substance, and forms a pretty experiment.

In two cases the dissolved gases were extracted from the sea-water in which the *ulva* was immersed (by boiling out with dilute sulphuric acid *in vacuo*) immediately after adding the polluting material, and again some hours later, and analyses made. The following results were obtained:—

Experiment 5A (Daylight).

Immediately after adding Ammonium Chloride. (0.180 part per 100,000). (C.c. per litre at N.T.P.).		Four Hours later.	
T = 14.4.		T = 15.9.	
O ₂	21.69		15.90
CO ₂	11.41		14.84
N ₂	9.79		9.88
Loss of CO ₂ = 5.79 c.c.		Gain of O ₂ = 3.43 c.c.	
The c.c. of evolved oxygen gas were also collected.			

Experiment 8E (Darkness).

Immediately after adding Effluent. (20 per cent).		Four Hours later.	
T = 14.6.		T = 14.8.	
CO ₂	63.59		66.44
O ₂	6.31		3.85
N ₂	11.90		11.74
Gain of CO ₂ = 2.85 c.c.		Loss of O ₂ = 2.46 c.c.	

In 5A the *ulva* had been in contact with the sea-water for a considerable time, whereas in 8E fresh sea-water was used.

The above analyses are interesting in several ways. First, in Experiment 5A, the amount of oxygen found is greatly in excess of the value given by Dittmar in the *Challenger* Reports for the volume of oxygen which one litre of sea-water can take up when saturated with constantly renewed air at the existing temperature, Dittmar's figure for 15° C. being 5.83 c.c. The action of the *ulva* is therefore, in a sense, to *supersaturate* the sea-water with oxygen under the existing conditions.

Secondly, the amount of carbonic anhydride found (in the same experiment) is much less than that present in normal sea-water, Dittmar's average for the total volume in sea-water being about 48 c.c. per litre, of which in all probability some 40 c.c. are in the form of soluble bicarbonate of calcium or magnesium. It is evident therefore that the *ulva* gains its carbon from the carbonic anhydride of these salts.

Thirdly, the results of the experiment in darkness demonstrate in an interesting manner the true respiration of the *ulva*, carbonic anhydride being evolved in practically the same amount as the oxygen disappearing.

THE EQUILIBRIUM LAW AS APPLIED TO
SALT SEPARATION AND TO THE FORMATION
OF OCEANIC SALT DEPOSITS.*

By E. FRANKLAND ARMSTRONG, Ph.D.

THE paper dealt with the application of the equilibrium law to the problem presented by the progressive separation of salts from solution, which is of special interest in discussing the formation of deposits of potash and other salts formed by the gradual drying up of ancient seas. The method was described of constructing models and diagrams representing the successive changes observed on concentration of solutions containing several inorganic salts.

For any given solution, *e.g.*, sea-water, it is possible from these models and diagrams to forecast the order in which the salts would separate from it on concentration, and also the relative amounts deposited at any stage. It was pointed out how the results obtained in this manner agreed almost exactly with the order and nature of the celebrated natural potassium magnesium salt deposits met with at Stassfurt.

* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

CONTRIBUTIONS TO THE SCIENCE OF
THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 167).

THE results of Thomas's test are analogous to those of the Abel test; in this also the product arising in the presence of nitrous acid gives the more favourable result.

It is worthy of note that, on repetition of the stability tests with the same material, the time period up to the beginning of the reaction becomes continuously greater. It would be expected that the repeated heating to 80° would rather have decreased the stability. The cause of the opposite result must be due to a slight diminution in the percentage of nitrogen in each sample tested, in consequence of which the explosiveness is lessened.

Experiment 2.—Two nitrations under similar conditions were again carried out. The one nitration mixture was free from nitrous acid; the other contained 0.28 per cent. The treatment of the nitration products was the same as in the previous experiment, only with this difference, that, on renewing the boiling water, the cotton liquid was poured through a filter, as the increase should be determined at this point also. In Experiment 1 this was

is therefore not identical with the product that, according to Lenk and Cross, causes the instability of gun-cotton. In any case, the formation of this substance has no connection with the nitrous acid, since it occurred in both products.

The material was now again absolutely white, and showed sufficient stability. In order to obtain a better conclusion as to the reliability of the test samples, two series of experiments were carried out, and in the same manner as in Experiment 1.

Thus, a diminution of the stability of gun-cotton through nitrous acid cannot be proved from these two series of experiments. Both products give coincident results in the stability tests. As in Experiment 1, the explosion-point of the gun-cotton obtained from the nitration mixture containing nitrous acid lies from 0.5° to 1° lower; but this slight difference leads to no satisfactory conclusion.

Both series of experiments afford coincident results, which is a proof that, by following exactly similar treatment in both cases, comparable values may be obtained.

With regard to the percentage of nitrogen, no difference of importance was registered. The determinations were carried out after completion of the boiling. Product *a* gave a nitrogen content of 20.8 c.c. NO; *b*, that of 20.8 c.c. But, before, on using a nitration mixture of 3 parts

FIRST SERIES.

Day of the experiment.	Without nitrous acid.		With nitrous acid.		Check experiment.
	<i>a</i> ₁ .	<i>a</i> ₂ .	<i>b</i> ₁ .	<i>b</i> ₂ .	<i>c</i> .
7/1/1900	15'	14'	17'	18'	15'
	E.P. = 186° 50'		E.P. = 186°		E.P. = 199°
	<i>t</i> = 4' 1"		<i>t</i> = 4'		<i>t</i> = 5' 40"
26/1/1900	37'	40'	41'	47'	15'
		E.P. = 186°		E.P. = 185° 50'	
		<i>t</i> = 4' 42"		<i>t</i> = 4' 40"	
3/3/1900	48'	47'	45'	51'	14'
	E.P. = 190°		E.P. = 188°		
	<i>t</i> = 3' 36"		<i>t</i> = 3' 34"		

Temperature of water-bath = 80°.

SECOND SERIES.

5/1/1900	15'	13'	15'	12'	16'
	E.P. = 186° 50'		E.P. = 186°		E.P. = 201°
	<i>t</i> = 4' 26"		<i>t</i> = 4' 25"		<i>t</i> = 4' 20"
3/2/1900	36'	34'	34'	35'	15'
		E.P. = 186° 50'		E.P. = 185° 50'	
		<i>t</i> = 5' 2"		<i>t</i> = 5'	
13/3/1900	47'	49'	51'	56'	15'
	E.P. = 191°		E.P. = 190° 50'		
	<i>t</i> = 3' 5"		<i>t</i> = 3' 4"		

omitted; there the material was simply poured on to a filter with fine holes, and, after the boiling was over, it was still quite white. In Experiment 2, however, the products gradually became brownish in colour, and after each washing upon the filter, at the renewal of the boiling water a small quantity of a brown substance collected beneath the filter. In the stability test, the test-papers were deeply coloured after three minutes. This bad result could only be traced to the presence of the brown substance. Both products were boiled again for a few times with water; in this case using the pump without filter-paper at each change of water, by which means the brown substance was removed in the washing. It was so small in quantity that an analysis was impossible, added to which it further contained white filaments from the gun-cotton. It could only be determined that this substance decomposed on ignition at 198° without effervescence, and showed itself insoluble in dilute acetone, and

concentrated sulphuric acid and 1 part concentrated nitric acid, 213—214 c.c. NO was obtained; therefore, during the protracted boiling, the percentage of nitrogen must have become lowered. According to Guttman, this also occurs in the manufacture of gun-cotton. In a research of Bruley's, on the other hand, after two hundred and sixty hours' boiling, the nitrogen content was only diminished by about 1 c.c. As in our case the material was cut up as finely as possible, it is possible that isolated filaments may have been thrown up on the sides of the vessel during boiling, and thus become over-heated. The same cause may perhaps be attributed to the formation of the previously-mentioned brown substance which diminishes the stability.

The determination of the increase was omitted for the reasons already mentioned, more especially as Lunge and Weintraub have already proved that it is not diminished even through an excessive proportion of nitrous acid, such as never occurs in practice.

From the above, we believe to have proved finally that,

* *Zeitschrift für Angewandte Chemie*, 1901, Heft 20.

for the manufacture of gun-cotton, the presence of nitrous acid in the nitric acid is of no significance. It may be again mentioned that our researches were carried out with pure cotton freed from fatty matter. The result thus obtained cannot, of course, without addition, be applied to the manufacture of nitroglycerin. From the great technical value of this question, a decision of this case also would have been desirable; but, unfortunately, the manipulation being considerably more difficult and dangerous than that of gun-cotton compelled us to abandon this research in a students' laboratory.

(To be continued).

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.*

By CHARLES BASKERVILLE.

ALMOST five years ago I attempted to separate thorium quantitatively from a neutral chloride solution by saturation with sulphur dioxide and boiling. As may be recalled, this was merely an application of the method formerly made known by me and used in the separation of zirconium (CHEMICAL NEWS, lxx., 57; *Journ. Am. Chem. Soc.*, 1894, xvi., 475) and titanium (*Journ. Am. Chem. Soc.*, 1894, xvi., 427). The separation of thorium by this means was not quantitative. On re-solution of the precipitated portion in hydrochloric acid and exact neutralisation with ammonium hydroxide and treatment again with sulphur dioxide, almost complete precipitation resulted, showing that the initial partial precipitation was not altogether due to imperfect action of the precipitant or the solubility of the basic thorium sulphite† in the neutral menstruum. This was verified by many repetitions of the process, using thorium chloride solutions of different strengths, and varying amounts of ammonium chloride.

These solutions were first made upon fairly pure thorium salts, prepared by me from oxides obtained from analyses of many monazite sands for the North Carolina Geological Survey (*Bulletin* 9, "Monazite and Monazite Deposits in N. C.," 1895). As this conduct was unexpected, and not in keeping with the observed reactions of the group, the experiments were repeated with thorium compounds obtained from different sources, with like results. I was favoured with several grms. of thorium sulphate prepared by Professor Dunnington, of Virginia, from monazite sand found in Amelia County, Va. Prof. Dennis, of Cornell, kindly gave me 3.5 grms. thorium nitrate (99.6 per cent pure); the hydroxide from which it had been prepared was separated by means of potassium hydronitrate (*Journ. Am. Chem. Soc.*, 1896, xviii., 947). I worked up about 5000 litres of thorium sulphate solution, obtained from Carolina monazite kindly collected by the late Mr. H. B. C. Nitze, Assistant State Geologist. The procedure followed need not be detailed here, as it will appear in a subsequent and more extended communication. Finally, Dr. Waldron Shapleigh generously gave me 2 kilograms. of the purest thorium oxalate to be had at the Auer Welsbach Works. My thanks are due these gentlemen for their kindness.‡

* Presented at the Denver Meeting of the American Chemical Society, August 27, 1901.

† These basic sulphites are being investigated at present. It may be well to state that, in addition to a flocculent basic sulphite, there has been obtained a gelatinous compound, or hydrogel, similar in appearance to the zirconium sulphite described by Venable and Baskerville (*Journ. Am. Chem. Soc.*, 1895, xvii., 448).

‡ While in the midst of re-purifying the compounds from such varied sources, and desiring to leave no stone unturned in the investigation, during the fall of last year I wrote Prof. Bohuslav Brauner, of Prague, of my observations, and requested a small amount of the purified thorium compound used by him in his excellent work on the atomic weight of that element (*Journ. Chem. Soc. Trans.*, London, 1898, lxxiii., 951). Very likely the letter went astray, as I have received no reply. I was surprised, therefore, to observe in the *Proceedings of the London Chemical Society* (April 10, 1901) an article by him on "Contributions to the Chemistry of Thorium,"

The purest thorium compounds were re-purified by the following procedure:—The sulphate was taken up in cold water, treated with sodium sulphate, and allowed to stand from twelve to twenty-four hours to ensure separation of the remaining cerium salts, the percentage of which was quite small. The liquid was filtered and the hydroxide precipitated in tall cylinders by large excess of chemically pure sodium nitrite. This precipitate was washed by decantation from six to ten times, using twenty volumes (to one of precipitate) of distilled water each time. To remove the last of the sodium salts and other soluble impurities, the precipitate was then dissolved in hydrochloric acid and re-precipitated by slight excess of ammonium hydroxide, and washed by decantation at least ten times, using twenty volumes of distilled water.

I. Variation in Specific Gravity of the Oxide.

The determination of the specific gravity of the oxides affords a rapid and excellent means of judging the rate of fractionation and, in a measure, the purity of the rare earths. This method has been especially urged independently by Muthmann and Böhm (*Ber. d. Deut. Chem. Gesell.*, xxxiii., No. 1; CHEMICAL NEWS, lxxxi., 181), as having time advantages over the necessarily long and often tedious equivalent determinations. Brauner also uses the method. The oxide obtained by prolonged ignition with the blast of the purified hydroxide obtained above had a specific gravity of 10.1 corrected to 4° C. Clarke, in his "Constants of Nature" (*Smithsonian Institution*, 1888, Part I., p. 48), gives the following values:—

Name and formula.	Sp. gr.	Authority.
Thorium dioxide, ThO ₂	9.402	Berzelius (<i>Pogg. Ann.</i> , xvi., 385).
	9.21	Nordenskiöld and Chydenius (<i>Fahresb.</i> , xiii., 134).
	9.077 } 9.200 } 9.861 }	Chydenius (<i>Fahresb.</i> , xvi., 194).
		Nilson and Petterson (<i>Comptes Rendus</i> , xci., 232).
	17° 10.2199 } (a) 10.2206 }	Nilson (<i>Ber.</i> , xv., 2536).
	15° 9.876	Troost and Ouvrard (<i>Comptes Rendus</i> , cii., 1422) †.

(a). Reduced to 4° C., this value is 10.201.

(b). Clarke gives a note stating that Nilson's determination is the only one of value.

About 10 grms. of the purified hydroxide obtained above were again dissolved in hydrochloric acid, made up to about 300 c.c., and exactly neutralised by dilute ammonium hydroxide. To ensure neutrality, the ammonia was added until the slightest permanent precipitate remained after stirring the cold solution vigorously for five minutes. The precipitate was separated by filtration, and the solution saturated with freshly-prepared and washed sulphur dioxide. Within a few minutes, a flocculent basic sulphite began to separate. As the reaction continued in the cold, the precipitate increased and then decreased somewhat. The solution was filtered cold and the filtrate

in which he gives good evidence of the complexity of thorium, dividing that element into Th α and Th β . Immediately at my first opportunity (April 23rd), at the Spring meeting of the North Carolina Section of the American Chemical Society, I made public mention of my work, which had been discussed in private often with others. Brauner's results were obtained by hydrolysis of the hepta-hydrated thorium tetrammonium oxalate. This communication contains, in part, the results of my experiments reported then and some observations made since. As soon as the unexpected properties were noted, almost five years ago, I indicated the differences by terming one Th and the other Th(X). It is deemed well to make this explanation in presenting a preliminary paper on incomplete work, as it was done independently, and the problem attacked in a different way. Results have been obtained which corroborate Brauner's work. It may also be stated that large quantities of the materials are being worked up, and the work will be pushed to a finality.

boiled, giving a second—but much smaller—precipitate, similar to the first; showing that the precipitate is soluble to some extent in the cold sulphurous acid solution. The hot filtrate was then precipitated with slight excess of ammonium hydroxide and filtered off. Portions of the sulphite and ammonia precipitates were removed from the funnels (care being taken that they were not contaminated with the ashless filter-paper), ignited in platinum crucibles with the blast, and the specific gravity of the oxides determined.

Before treatment	10.1
Sulphur dioxide precipitate	9.58
Soluble portion precipitated by ammonia	10.367

(All determinations here and elsewhere in this paper were corrected to 4° C.).

Twenty grms. of Shapleigh's purest thorium oxalate were re-purified according to the method given above. A saturated solution of chemically pure citric acid was prepared, and the pure hydroxide added in excess, *i.e.*, until no more was dissolved cold when the stirring had continued (by means of a motor) for from twelve to fifteen hours (different experiments). In attempting to concentrate the filtered solution by heat, a heavy white precipitate—resembling, in a measure, barium sulphate in appearance—came down. The utmost care was necessary in boiling the solution, as the bumping was often quite violent. The precipitate re-dissolved when the solution was cooled. In evaporating the solution on the water-bath, the precipitate appeared and was dissolved again on cooling.

A thorium citrate is described by Chydenius (*Pogg. Ann.*, 1863, cxix, 55; "Kemisk undersölening af Thorjord och Thorsalter," Helsingfors, 1861), but he did not investigate it further than to determine the percentage of oxide present. The investigation of this citrate, not previously noted, is well under way, and will be published later as a separate paper. For our purpose here, it suffices to state that the precipitate may best be obtained and separated by diluting the solution from five to ten times, and holding it at—or just below—100° C. This has been done by placing the large beaker (Jena glass) in a boiling water-bath for an hour. The precipitate settled well, and the clear supernatant liquid was decanted; the precipitate was washed several times with boiling water by decantation, the settling occurring while the beaker was surrounded by boiling water. Finally, the precipitate was thrown upon a large filter-paper and washed several times with boiling water, or until the wash-water was only faintly acid to litmus. The precipitate was carefully removed from the funnel, avoiding contamination with fibres of the filter-paper, brought to a constant weight at 105° C. in an air-bath. Prepared thus, the body is a beautiful white heavy amorphous powder, and is a hydrated citrate of the real thorium.

Portions of this purified citrate made at different times were ignited in platinum crucibles with blast and the specific gravity of the oxides determined.

Amount oxide taken.	Sp. gr. corrected to 4° C.
0.1989	9.254
0.6000	9.253
0.3830	9.210
0.4166	9.188 (a)

(a). Citrate prepared from second heating of one of the solutions which was not completely precipitated at first.

From these determinations, it appears that Nordenskiöld and Chydenius very likely at one time had the nearly pure thorium compound. I am inclined to the opinion that the oxide obtained by me above is still not quite pure, for reasons given below (see also "Radio-active Experiments"). One of the regrettable features of the paper is that I am unable yet to submit the results of the spectroscopic investigation of the material. Preliminary atomic

weight determinations have been made from this oxide, however.

The filtrates (without the wash-water) obtained from the citrate mentioned above were concentrated in platinum on a water-bath. As the solution became concentrated, a little more of the insoluble citrate separated out, but in one series of the experiments no effort was made to separate it, but the whole carried down to a thick syrup and allowed to cool, when it became a mass of solid crystals, more or less opaque from the insoluble citrate bound up with the mass. Two grms. of this material were ignited, and the specific gravity of the oxide determined.

Oxide taken.	Specific gravity.*
0.4000	10.50

A larger quantity of the saturated citrate solution was prepared, and most of the insoluble citrate removed according to the method given. About 2 litres of filtrate (wash-water not included) were concentrated to 400 c.c. in platinum on the water-bath, when a crystalline scum began to form. The dish was covered and allowed to stand over night. A few heavy crystals separated at the bottom. The thick syrup was drained from the crystals, which, without crushing, were washed three times with water, dried at 120° C. On ignition, 31.61 per cent of oxide was obtained. Specific gravity of the oxide was determined.

Oxide taken.	Specific gravity.
0.1789 gm.	8.77
0.2024 "	8.47

What this oxide is I am unable to say, unless it be the new body recently reported by Hofman and Prandl (*Ber.*, 1901, xxxiv., 1064) as a contamination of zirconium in euxenite. It constitutes only a very small percentage of the thorium, and demands careful investigation, which I cannot at present undertake on account of the wealth of other material demanding more immediate attention. I should like to have the privilege of investigating it later, however.

When the syrup obtained above was further evaporated to about 300 c.c., a white crystalline body separated, and formed a thick coating on the bottom of the dish. The liquid was decanted; the crystals washed until the water was only faintly acid, and dried at 120° C. The residue amounted to 16.20 per cent after ignition, and had a specific gravity of 10.14 using 0.3820 gm. of oxide.

On continued concentration small crops of crystals were obtained, consisting primarily of citric acid with decreasing percentages of oxide. These salts have not yet been closely studied. When the syrup was brought to about 200 c.c., it was diluted approximately to a litre and boiled. A small precipitate, very similar to the first insoluble thorium citrate, yet different, was obtained. The oxide obtained when the material was ignited was exceedingly white.

Oxide taken.	Specific gravity.
0.1812 gm.	11.26

As the quantity of the material obtained was very small, too much weight should not be given to this value.

Two portions of the filtrate from this precipitate were evaporated to dryness in a platinum dish, ignited, and the specific gravity of the residue determined.

Oxide taken.	Specific gravity.
I. 0.5566 gm.	10.46
II. 0.8316 "	10.53

II. was strongly ignited in a covered platinum crucible for three hours.

These determinations prove the presence of an oxide having an unusually high specific gravity, which cannot be accounted for except by the presence of either a new oxide of a known element having greater density than

* Mr. R. O. E. Davis, Assistant in the Laboratory, aided in some of the physical constant determinations. He is at present at work on the citrates and molybdates.

the usual non-volatile residue after ignition, or an unknown element. It is needless to say that the absence of such heavy substances as lead from the reagents was proven. From the variation in the values, assuming no error in manipulation, the oxide is not yet pure; but careful fractionation, using much greater quantities of the material, gives good promise.

II. Experiments on the Radio-activity of the Oxides.

In writing of the now well-recognised Becquerel rays M. and Mme. Curie (*Comptes Rendus*, cxxvii., 175; *CHEM. NEWS*, 1898, lxxviii., 49) say that "the property of emitting rays . . . which act on photographic plates is a specific property of uranium and thorium." Sir William Crookes (*Proc. Roy. Soc.*, lxvi., 499) has practically proven that the radio-activity of uranium is due to a constant constituent, which can be partially fractionated out, $Ur(X)$. In the same paper Sir W. Crookes presents the results obtained in a few preliminary experiments he made to separate thorium compounds into an active and inactive body (*loc. cit.*). His experiments in fractionating thorium sulphate gave negative results. However, when he obtained six fractions by crystallising the nitrate, the oxide from the first end crystals gave a feeble action, while the other end "gave an impression about three times as intense. This points to the possibility of separating from thorium its radio-active substance" (p. 421). My own experiments are in exact accord with the above. The oxide (9.25 sp. gr.) obtained from the insoluble citrate affects the sensitive plate in the dark after an exposure of seventy-two hours but slightly, while the oxides of higher specific gravity are quite active. A number of plates have been exposed using oxides obtained throughout the research, monazite sand from which the thorium salts were prepared, uranium nitrate, acetate, uraninite, and blanks for comparison. The radio-activity increased with the increase in specific gravity. For reasons given below I am of the opinion that the 9.25 thorium oxide is not quite pure, that is, free from traces of the higher oxide; hence, its faint activity. (See above; method of application is outlined below).

I am not yet ready to assert that the new substance obtained is not the third radio-active body reported by Debiere in pitchblende, actinium (*Comptes Rendus*, October 16th, 1899, and April 2nd, 1900; *CHEM. NEWS*, lxxxi., 169), which he states belongs to the iron group. From Madame Curie's statement, Debiere supposes "that the radio-active property observed in thorium compounds does not belong to this element, but is due to a foreign material," hence actinium? From Rutherford's experiments on induced radio-activity, one is loath to accept the radio-activity of unprotected bodies as sufficient evidence of their sameness. I have not, so far, had time to apply the radiant matter test, but amassing chemical evidence, so far obtained, points to the presence of a hitherto unrecognised body.

An account of the method used in these preliminary experiments on the radio-activity of thorium and its constituents may be of interest. The plan was essentially the same followed by Sir W. Crookes (*loc. cit.*), differing somewhat in details. Placing small circular pill-boxes containing the materials directly on the same sensitive plates was not satisfactory on account of the excessive radiation from the concentrated active body in all directions. Black glazed paper, the size of the plate, was punctured with circular holes about 1.5 c.m. in diameter, and placed dark side up on the plate. A sheet of silver-free lead, about 0.5 m.m. thick, was similarly cut and placed on the paper, which served to protect the plate. The material was placed in quantities varying from 0.25 to 1 grm. in small exhibition glass tubes 1 c.m. in diameter and 5 c.m. tall. These cells were closed by sealing thin circular microscope slide covers to the flange with Canada balsam. After air-drying, the cells were inverted, and the sealed end placed neatly over the circular openings in the lead and paper, thus exposing portions of the plate to the

radiant action downward through a thin medium of glass and air, as the cells were not in contact with the sensitive surface nearest the tubes being held up by the flange, which projected beyond the circular opening. To eliminate lateral radiant action, each cell was then surrounded by a cylinder of lead, which was filed to fit snugly upon the sheet lead below. These cylinders were about 2.5 c.m. in diameter inside, and 5.25 c.m. high. Such a battery, having from two to eight cells differently charged, was placed in a box, closed, covered with black glazed paper, several thicknesses of cloth, and locked in a dark room for various lengths of time, twenty-four to one hundred and forty-five hours. The plates were afterwards developed. Similar experiments were carried out, placing the ordinary black paper, usual covering of plates, between the cells and the sensitive surface without puncturing the paper. The active oxides affected the plate through the paper medium.

(To be continued).

THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.*

By JOSEPH W. RICHARDS.

WHEN Harkort, a Freiberg student, invented the quantitative blowpipe assay for gold and silver, in 1824, he was at once confronted with the impossibility of weighing the very small buttons obtained. He surmounted the difficulty by assaying a silver ore repeatedly in the muffle, until he knew with exactness its contents. Then he assayed a standard weight of it by the blowpipe, and obtained a button of a certain size, whose weight was known from the amount of ore taken. Taking half and a third and a quarter of the weight of ore he obtained smaller buttons of known weight. With these he constructed a scale. He drew two fine slightly diverging lines on white cardboard, placed the buttons between the lines at the points where they fitted, and marked opposite those points the corresponding weights, or, rather, the corresponding silver contents of the ore, assuming a standard weight taken for assay.

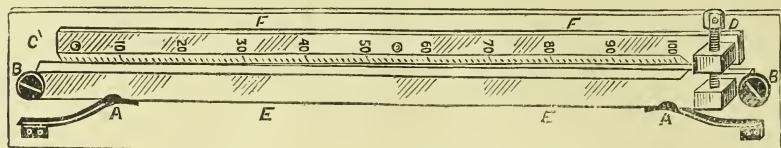
Harkort brought the method to the attention of Plattner, the professor of metallurgy at Freiberg, and published his results at his own expense in a small book entitled "Silverprobe vor dem Löthrohr," Freiberg, 1827.

Plattner took up this method in his regular course of instruction, and improved and extended it. One of his principal improvements was the construction of the button scale rule on ivory, made by the mechanic August Lingke, at Freiberg. To fix accurately the dimensions of this scale, Plattner assayed a very rich silver ore repeatedly in the muffle until it was known with certainty to contain exactly 3.48 per cent of silver. He then made repeated blowpipe assays of this ore, obtaining buttons very close together in size and weight. The two lines were then drawn on ivory so that they diverged approximately the diameter of these buttons in 150 m.m. The buttons were then fitted exactly between the lines, and the point marked 50, the distance from here to the meeting point of the lines being divided into fifty equal divisions. The exact dimensions of the scale as thus made were 156 m.m. from 0 to 50, and the lines 0.9 m.m. apart at 50. The weights corresponding to the various numbers were calculated from the number 50 representing 3.48 m.grms. of silver (when 100 m.grms. were taken for analysis), using the assumption that as the buttons were nearly spheres, or, at least, were homologous in shape, their weights would vary as the cubes of their respective horizontal diameters. The weight of the silver button corresponding to any number from 1 to 50 would be therefore—

$$3.48 \times \left(\frac{n}{50}\right)^3,$$

* *Journal of the American Chemical Society*, xxiii., No. 4.

and thus these weights were all calculated and engraved on the scale opposite the numbers. A similar set of weights was obtained in an exactly similar manner for gold buttons. Thus the Plattner ivory scale was devised, and is still used more extensively than any other method of measuring these small buttons.



The defects of the Plattner scale may be enumerated under the heads of:—

1. Errors in construction.
2. Errors in using.

The errors in constructing the scale may be as follows:—

- a. The lines are sometimes not mathematically straight.
- b. The lines may be rough or ragged.
- c. The lines may not meet exactly at the point marked zero.
- d. The lines may not be exactly the right distance apart (0.9 m.m.) at the point marked 50.

It is seldom that the best scales made in Freiberg are free from one or more of these defects; I do not believe that more than one out of five is perfect.

The errors in using the scale consist of:—

a. Placing the button too high or too low through optical illusion. The button should be tangent to the inside of the lines, and in a strong light the white metallic surface of the button is difficult to see on its outer edge. One investigator has even proposed putting the silver buttons a short time into ammonium sulphide, so as to blacken them, and thus facilitate their measurement.

b. Placing the button too high by virtue of parallax, which projects the middle diameter of the button against the scale on which it rests, and makes the button seem to fit higher up than its real diameter. The remedy for this is to sight first down one side of the button, then down the other, each time looking perpendicularly to the scale. This operation is tedious, and takes considerable experience.

c. The button being nearly round, it takes considerable time, patience, and experience to get it to a certain spot on a flat surface. This is not an error of the scale, but an unavoidable inconvenience, which becomes accentuated if the ivory warps, so that the scale does not lie level. A beginner will frequently make a greater mistake in measuring a button than in getting it.

Goldschmidt's Method.—Dr. V. Goldschmidt, of Heidelberg, proposed two improvements:—

1. *To Re-melt the Cupelled Buttons on Charcoal.*—This gives to them a more nearly spherical and more uniform shape than is obtained on the cupel. The button is to be removed from the cupel, hammered flat between paper, to clean it, and then touched with the reducing flame, on charcoal, just long enough for it to melt and take the spherical form. Buttons thus re-melted will be heavier than cupelled buttons of the same horizontal diameter, and, therefore, heavier than the given weights on the Plattner scale.

2. *Measuring the Horizontal Diameter of such Re-melted Buttons under the Microscope.*—For this purpose, a divided scale is put into the focus of the eye-piece of a compound microscope magnifying 50 to 100 diameters. A scale of 40 divisions is very suitable, the tenths of each division being estimated when measuring. The buttons are placed on a glass plate, a piece of blue glass gives a nice background, and since they come to rest only on their bases, the horizontal diameter is always in position to be measured. The diameter being known in whole divisions and tenths, reference to a previously constructed

table gives the volume and weight of the button, when of gold or silver.

To construct this table, the following ingeniously devised plan was worked out by Goldschmidt:—A number of bits of pure gold are melted on charcoal. The buttons obtained are each measured separately, in divisions on the

scale. All the buttons are then weighed together, as accurately as possible. The total weight, divided by the specific gravity of gold, gives the sum of the volumes of the buttons. This latter divided by the sum of the cubes of the separate diameters (expressed in divisions on the scale) gives a function μ . This function is the factor by which to multiply the cube of the diameter of any button to get its individual volume. Expressed algebraically, the above operations are:—

$$\frac{\Sigma \text{ weight}}{\text{Sp. gr. gold}} = \Sigma \text{ volumes.}$$

$$\frac{\Sigma \text{ volumes}}{\Sigma (\text{diam.})^3} = \text{a function} = \mu.$$

Volume of any button = $\mu \times (\text{diam.})^3$.

Weight of a gold button = $\mu \times \text{sp. gr. gold} \times (\text{diam.})^3$.

Weight of a silver button = $\mu \times \text{sp. gr. silver} \times (\text{diam.})^3$.

From the above data, a table can be constructed showing the weights of gold or silver buttons for every division of the scale up to its full range.

It should be remembered that measurement under the microscope is a very satisfactory laboratory method, but as it requires a compound microscope, it is not suitable for field use or prospector's outfits.

Richards's Scale.—The writer adopts Goldschmidt's idea of re-melting the button on charcoal, wherever practicable, but has devised a modification of Harkort's method for measuring the buttons.

The idea is to make two metallic edges perfectly straight, lying on a flat surface, touching each other at one point, and held apart at the other extremity by a set-screw, so that the point 100 may indicate a fixed width or separation of almost exactly 1 m.m. In reality, the button whose horizontal diameter fits at 100 has a diameter of 1.02 m.m., but this distance has been so chosen that the volume and, consequently, the weight of said button are exactly that of a perfect sphere whose diameter is 1 m.m. The other numbers on the scale have the same significance; for example, the button whose horizontal diameter fits at 43.5 has the volume and weight of a sphere whose diameter is 43.5 hundredths of a m.m., and such is the basis on which the table is calculated.

In using the scale, the button is put into the groove, the scale inclined slightly, and tapped until the button wedges itself. The tenths of a division are estimated, taking the points where the sides of the button touch the scale as the reading. As the button may sometimes roll with its shorter vertical diameter across the scale, several readings are taken, and the highest reading occurring with regularity is the true horizontal diameter. For instance, among 43.4, 43.4, 41.6, 43.5, 41.8, 43.5, it is evident that 43.5 is the horizontal diameter, and 41.6 or 41.8 the vertical. The button can also be observed under the lens, to see how it is lying, at any given reading.

A gentle spring keeps the right-hand strip against the set screw, thus allowing it to be pressed back for cleaning out the slot with a brush or removing a button. The scale is made of hardened aluminum, for lightness, and is set in a velvet-lined leather case. It is made by Williams, Brown, and Earle, of Philadelphia, and sold at the same

price as the imported ivory Plattner scales. P. Stoë, of Heidelberg, makes and sells the scales in Germany.

The advantages of this method of construction over the engraved ivory scale are:—

1. The edges are perfectly straight, from the method of construction.

2. They meet exactly at the zero point, and can be adjusted to the exact distance at 100.

3. The reading is more or less automatic, the errors of placing, parallax, and personal equation being almost entirely eliminated.

The scales are adjusted by the makers, but, if by accident they get out of adjustment, a small rod of wire furnished with each instrument, whose lower end marks a given reading on a correct instrument, provides the means of quick re-adjustment.

Measuring Gold-Silver Alloy Buttons.—When the button obtained is pure gold or pure silver, any of the above methods give its weight directly. If, however, it is an alloy of the two, and is too small to weigh satisfactorily, but must be measured, the question of determining the silver present as well as the gold is a difficult one. The determination is very much facilitated by using the small case of standard alloys designed by Dr. Goldschmidt, of Heidelberg (made by P. Stoë, Heidelberg, imported by Williams, Brown, and Earle, Philadelphia). This is a small tablet in a brass case, containing small flattened buttons of gold-silver alloys, every 1 per cent of silver to 20, then every 2 per cent to 40, and every 4 per cent to 56, where the alloy becomes silver-white. In using, the alloy button to be tested is hammered flat between paper, put on the plate, and examined under the lens by diffused daylight. With a little experience, the button can be placed to one alloy. The observation gives the per cent of silver in the button. Assayers working by the muffle will also find this a very convenient instrument to save parting where a quick, approximate determination is wanted, or to determine how much silver to add to an alloy to get the right proportions for nitric acid parting.

I have classified the different methods available to the blowpipe assayer as follows:—

I. If the button is over 50 per cent of gold, and therefore coloured, melt on charcoal, measure, and note its volume. Then proceed by either of the following methods:—

(a). Flatten out, compare with the standard alloys, and get the per cent of silver in it. From the table of specific gravities of gold-silver alloys take the specific gravity. Multiply the volume of the alloy by its specific gravity; the product is its weight. From the known percentage of silver and gold in it, calculate their respective weights.

(b). Melt the button with a button of pure silver having an equal diameter, if the colour of the alloy is pale; or of 25 per cent greater diameter, if the colour is brass-yellow; or of 50 per cent greater diameter, if of nearly pure gold colour. Hammer out flat, and part with nitric acid in the usual way. Wrap the gold in a small piece of pure lead foil, cupel, re-melt, measure, and thus get its weight and note its volume. Subtract the volume of the gold from the volume of the alloy, and the difference is the volume of the silver. The weight of silver corresponding to this volume is obtained directly from the table.

The writer has verified these two methods of procedure, and found them both reliable. The principle of method (a) is due to V. Goldschmidt, but not exactly in the simple form given above. The principle of method (b) is based on the fact that gold and silver neither contract nor expand in alloying, which fact the writer has verified by experiment and calculation.

II. If the button is less than 50 per cent gold, and therefore silver coloured. Melt on charcoal and note its volume. Then proceed by either:—

(a). Part with nitric acid (re-melting with more silver if not attacked). Wrap the gold in lead foil, cupel, re-melt, measure, note its weight and volume. Subtract its volume

from that of the alloy, getting the volume of the silver, and thence its weight.

(b). Measure accurately a pure gold button of approximately the same diameter as the alloy button. Melt together on charcoal, and measure carefully, noting the volume. Flatten out (the colour will be yellow), compare with the standard alloys, and, knowing the volume, compute the weight of gold and silver present. The weight of gold found, less the weight of the gold button added, gives the weight of gold in the original assay button. The weight of silver may be obtained by calculation from either the original alloy button or the yellow one after gold had been added.

This method of procedure was suggested by Professor B. W. Frazier, of Lehigh University.

(c). Replace on charcoal, and heat intensely in the point of the oxidising flame. The silver slowly volatilises, and in one to five minutes the alloy becomes yellowish. It is difficult to drive all the silver off, as the last 5 or 10 per cent volatilise slowly, and probably also take a little gold with them. It is best to stop when the alloy has a pronounced yellow colour, measure, note the volume, flatten out, compare with standard alloys, and calculate the weight of gold present. Take the volume of that weight of gold from the table, subtract from the volume of original alloy button, and thus obtain the volume and thence the weight of the silver.

The fact that silver can be volatilised from gold in this way, on charcoal, was described by the writer in the *Journal of the Franklin Institute*, June, 1896.

The writer finds methods I. (a) and II. (c) the most suitable for field work; the parting with nitric acid is preferably a laboratory method, and is the most accurate.

(To be continued).

CORRESPONDENCE.

CHEMICAL NAMES IN BOTANY.

To the Editor of the Chemical News.

SIR,—It may interest some of your numerous readers who may not be aware of the fact, that in the botanical family of the *Melastromaceæ* (established by Jussieu, Bonpland, and Robert Brown), which has been very carefully studied by De Candolle, two genera are dedicated respectively to Lavoisier and Humphry Davy.

None of the plants of this extensive group are natives of our English climate; they are mostly large trees of the hot regions of the globe.—I am, &c.,

T. L. PHIPSON, Ph.D.

Casa Mia, Putney, S.W.,
October 7, 1901.

OCCURRENCE OF MANGANESE IN WATERS.

To the Editor of the Chemical News.

SIR,—Some little time ago I had occasion to enquire into the cause of a dark brown sediment in a town's water supply, which was giving considerable trouble and inconvenience to consumers.

The first sample which I received was found to contain about 70 per cent of hydrated manganese oxide, the remainder being principally carbonate of lime and organic matter. This result was looked upon with doubt, as the sample had been taken from a source where the contamination of manganese ore, in the form of dust, was not at all impossible. Further samples were then taken right at the very source of the water supply, and these were found to corroborate the existence of manganese in estimable quantities (0.25 grain per gallon hydrated manganese oxide). The water is pumped up from wells in the red sandstone, and is perfectly clear and colourless, and in

every respect a wholesome water. In places down the wells where the water flows over the sandstone there is the same dark brown deposit of hydrated manganese oxide mixed with calcium carbonate, and in pipes which have been laid some years a considerable deposit of the two substances is found.

I have searched in many volumes of the *CHEMICAL NEWS* and other scientific journals, but can find no record of the occurrence of manganese in waters. Although the amount found in this case is fairly large, it might very possibly have been overlooked in an analysis of the total solids, as compared with the carbonate of lime it would be relatively small.

The manganese appears to exist as a bicarbonate (though this is not certain); it is at once precipitated along with the lime on boiling the solution. When dealing with large quantities, this can be easily seen forming a slight brownish scum on the surface during evaporation.

I venture to trouble you with an account of this experience in the hope that it may prove of interest to some of your readers, and also because it is either an unusual case, or else the occurrence of manganese in waters is apparently overlooked. If a similar case has been noted by anyone, I shall be pleased to compare notes with him.—I am, &c.,

T. H. BYROM.

NOTICES OF BOOKS.

Commercial Organic Analysis. By ALFRED H. ALLEN, F.I.C., F.C.S. Third Edition. Volume III., Part I. *Tannins; Dyes and Colouring-matters; Writing Inks.* Revised and Edited by J. MERRITT MATTHEWS, Ph.D. London: J. and A. Churchill, 1901. Pp. 589.

THE growth of our knowledge of organic analysis has necessitated a considerable alteration in the arrangement in this new edition of Vol. III., Part I. In the previous edition, this part dealt with the aromatic acids. This subject has now, however, been transferred to another volume, and the one now before us is entirely devoted to tannins, colouring-matters, and writing-inks. These sections have been much amplified, and a great deal of the old material has been re-written. New methods are described, as well as improvements in the old ones. It is to be regretted, as pointed out by the reviser, that our knowledge of tannin analysis is still so uncertain that two methods very rarely give concordant results.

The classification of dyes and colouring-matters has been changed, and the amount of matter given almost doubled; while the method of tabulated reactions adopted must reduce the work of testing by a very great deal.

It is to be regretted that there is rather a long list of errata; many of these may be classed as printers' errors, but some are of real importance—such as for "acid," read "alkali"; for "soluble," read "insoluble."

In a work of this magnitude, it is difficult to pick out any particular points for special notice. The volume teems with valuable information and new methods of procedure. The book is well printed, and bound to match the preceding volume, to which it makes a valuable companion.

The Self-Educator in Chemistry. By JAMES KNIGHT, M.A., B.Sc., F.C.S., F.G.S., F.E.I.S. Edited by JOHN ADAMS, M.A., B.Sc., Rector of the Free Church Training College, Glasgow. London: Hodder and Stoughton, 27, Paternoster Row. 1901.

THE above work is not intended as a preparation for examination, or for students at all in the narrow sense of the term; but recognising the importance of a certain amount of chemical knowledge in every department of life, the author has endeavoured by his book

to give a ready means whereby any ordinary person with a desire to become acquainted with the subject can grasp the fundamental principles of chemistry. A number of experiments of simple character are introduced with minute instructions for carrying them out. The author describes his book as an attempt to dispel a little of the "superstitious dread which surrounds the word chemical," an attempt in which we think he has been fairly successful. The first two chapters on the atomic theory and chemical nomenclature are particularly clear, and would be found useful even to students preparing for an examination. Considering that the outlines of both organic and inorganic chemistry are included in 160 pages the subjects are necessarily treated briefly; but the descriptions and explanations are original and clear. There is a table of contents and a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., Nos. 9, 10, and 11.

These three numbers contain no chemical matter.

No. 12, September 16, 1901.

The Molecular Weight of Chloral Hydrate at the Temperature of Ebullition.—M. de Forcrand.—The author applies the rule which he recently discovered (*Comptes Rendus*, vol. cxxxiii., p. 368) to the case of certain compounds which dissociate more or less completely at their boiling point. He first considers the case of chloral hydrate, for which substance the necessary thermochemical constants are almost all known. He admits, as a first approximation, a complete dissociation at boiling point (96.5° C.). M. Berthelot gives the values $L = 21990$ cal., and $S = 5500$ cal., from which

$$\frac{L + S}{369.5} = 74.1.$$

This number, 74.1, is more than double the mean 30, but, assuming the author's hypothesis, this should be the case for two reasons. First, the hydrate has been completely separated into water and chloral; there are now two molecules and the mean value of the quotient ought to be 60. Secondly, the number 21990 cal. is in reality the heat of volatilisation, together with the heat of combination (+6230 cal.); disregarding this latter number, the value 5730 is obtained, a number comparatively near to 60. The fact of its being too low apparently shows that dissociation is not absolutely total, and this result confirms M. Berthelot's experiments. At the temperature of ebullition the vapour of chloral hydrate contains water, chloral, and a little non-dissociated hydrate.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Microscopical, 7.30. Exhibition of Mounted Specimens of Marine Zoological Objects, by C. L. Curteis, F.R.M.S. "The Fungi Found on Germinating Farm Seeds," by Miss A. Lorrain Smith.

HARRIS INSTITUTE, PRESTON.

LECTURER IN CHEMISTRY.

The Harris Council invite applications for the Post of LECTURER IN CHEMISTRY. Salary £150. Further particulars may be obtained on application to the Secretary. —Applications, with copies of not more than three recent testimonials, should be sent in on or before Wednesday, October 16th, 1901, addressed to the undersigned.

F. R. JOLLY, Secretary.

THE CHEMICAL NEWS

Vol. LXXXIV., No. 2186.

ON THE DISTRIBUTION OF CHLORINE IN YORKSHIRE.*

PART II.

By WILLIAM ACKROYD, F.I.C.

ALL figures refer to parts of chlorine per 100,000 of water. As the result of many observations of minima the chlorine is found to increase from 0·7 up to 1, in the west and north-west, where the rivers originate, to 1·7 up to 2 in the east and south-east, where, in the Chalk Wolds, the up-turned edges of the chalk drink in and store up a vast amount of rain-water which is utilised by many of the East Riding communities. Beyond this there is a south-eastern area of high chlorine figures formed by the triangular tract of drift ending with Spurn Head; a pump at Paull near the Humber side gave 117·5; a Withernsea well in the drift gravel, 24·4; Hambleton station, 17; Hedon and Ryehill stations, each 16·5. The lowest figure obtained in this area was 2 at Driffild, Hesslewell, and Selby.

Every large centre of population has a high disturbing influence on the normal chlorine for the neighbourhood, which is shown by the chlorine figures yielded by the rain-water. The Massachusetts Board of Health (1890, [1], 680) found that twenty persons per square mile will add, on the average, 0·01 part of chlorine to the water flowing from the district. Such an estimate must have a purely local application on account of the inverse relation existing between the quantity of chlorine and quantity of water, which is pointed out in another paper (CHEM. NEWS, vol. lxxxiv., p. 176), and also because of the wide variation of these quantities from various causes. The following is a comparison of the averages for three months winter (1900—1901) rainfall for town and country in Yorkshire:—

Contents of rain-gauge in a manufacturing town (Halifax); average of 51 samples	2·38
Contents of moorland rain-gauges at Widdop, Walshaw Dean, Warley, Ovenden, and Midgley in Yorkshire; average of 68 samples	1·37
Excess of town over country	1·01

That part of the borough of Halifax in which the rain-gauge is kept forms a catchment area of 2·03 square miles, and comprises some seven wards with a population of 59,185. Its contribution of chlorine (1·01) through the rain is therefore 0·01 per 288 people per square mile; but the total contribution from air as well as ground in this closely populated district is 0·01 part of chlorine per 53 people per square mile, taking the maximum ground water figure as 5·5. (See *B.A. Report*, 1900, p. 685, and CHEM. NEWS, vol. lxxxii., p. 162).

The influence of high winds has direct bearing on the subject. This is shown in plotted diagrams for the three months' observations, where there are two well marked chlorine peaks which synchronise in the four curves, one for the week ending December 24th, 1900, and the other for the week ending January 14th, 1901. In the former week westerly gales prevailed, and presumably the chlorine maximum is evidence of marine influence; the wind acquired its greatest velocity on the 20th December of 43 miles per hour. In the January week strong continuous east winds blew from the German Ocean with a

very light rain or snow-fall, a combination again calculated to send up the chlorine to an abnormal height; the highest velocity reached was 27 miles per hour E.N.E. on the 9th, and 25 miles on the 7th January. The velocities are those taken at Stonyhurst College Observatory, the nearest point to the moorlands on the Lancashire side, and have been kindly supplied by the Rev. W. Sidgreaves.

THE RELATIVE PROGRESS OF THE COAL-TAR INDUSTRY IN ENGLAND AND GERMANY DURING THE PAST FIFTEEN YEARS.*

By ARTHUR C. GREEN, F.I.C., F.C.S.,
Consulting Chemist and Chemical Engineer.

THE coal-tar colour manufacture has well been called the flower of the chemical industries. Although in absolute money value of its products not equalling some other branches of industrial chemistry, it represents the highest development of applied chemical research and chemical engineering, and may well be taken as the pulse of the whole chemical trade. For a country which allows the most scientific branch of chemical industry to languish cannot expect to maintain pre-eminence for long in any simpler branch of chemical manufacture, since the skill trained for attacking the difficult problems of organic chemistry is certain, sooner or later, to be brought to bear on the simpler questions presented in the manufacture of so-called "heavy chemicals" (acids, alkalis, bleach, salts, &c.), and processes hitherto often left to the supervision of foremen will be taken in hand by educated chemists, with consequent improvement in methods of manufacture, better yields, purer products, and cheaper production. The importance of the coal-tar industry cannot, therefore, be estimated alone by the value of its products, for it exerts a widespread effect upon all other branches of chemical manufacture, from many of which it draws its supplies of raw material. As a pregnant example of this influence, which has been especially noticeable during the last decade, I may mention the revolution which is taking place in the manufacture of sulphuric acid, that most important product of the "heavy" chemical trade. A strong demand had arisen in the colour industry for a large and cheap supply of sulphuric anhydride chiefly in connection with the manufacture of alizarine colours and of artificial indigo. With the object of satisfying their own requirements in this respect the Badische Aniline and Soda Works of Ludwigshafen devoted much time and research to the problem of improving the catalytic process usually known by the name of Winkler, a modification of which process had been worked in this country by Squire, Chapman, and Messel since 1876. This endeavour was attended with such success that by means of the process and plant which they finally evolved, they were enabled to produce sulphuric anhydride so cheaply that not only could it be used as such for a large variety of purposes, but, by combination with water, afforded a profitable source of sulphuric acid. This new method of manufacturing sulphuric acid is, for concentrated acid at least, cheaper than the chamber process, and since the product is absolutely free from arsenic and can be produced at any desired concentration, it seems likely to supplant eventually the time-honoured method of manufacture.

Besides exerting a stimulating influence upon the inorganic chemical manufactures, the coal-tar industry has given birth during recent years to several important daughter industries. The manufacture of synthetic medicinal agents, artificial perfumes, sweetening materials, antitoxins, nutritives, and photographic developers are all outgrowths of the

* Read before the British Association (Section B), Glasgow Meeting, 1901.

* Read before the British Association (Section B), Glasgow Meeting, 1901.

coal-tar industry, and in great part still remain attached to the colour works where they originated. Of these subsidiary industries the most important is the manufacture of synthetic medicinal preparations, which has already attained to large proportions, and bids fair to revolutionise medical science. The requirements of the coal-tar industry have further led to great advances in the design and production of chemical plant, such as filter-presses, autoclaves, fractionating columns, vacuum-pumps and stills, suction-filters, enamelled iron, aluminium, and stone-ware vessels, &c., for the supply of which extensive works have become necessary.

It is a frequently quoted remark of the late Lord Beaconsfield that the chemical trade of a country is a barometer of its prosperity, and the chemical trade of this country has always been regarded as a most important branch of our manufactures. Even those who might be inclined to regard our declining position in the colour industry with more or less indifference would consider the loss of a material portion of our general chemical trade as nothing less than a national calamity. As already pointed out, however, the two are indissolubly connected, the coal-tar industry being an essential and inseparable part of the chemical industry as a whole. It is with the object of ascertaining our present and future prospects in the chemical trade of the world that I propose to compare the relative development of the colour industry in England and Germany during the past fifteen years. It was at the commencement of this period, that is to say in the year 1886, that Professor Meldola in a paper read before the Society of Arts, gave a masterly account of the position of the industry in this country at that date, and sounded a warning note to our manufacturers and business men regarding its future progress. If an excuse is required for my venturing to refer again to a subject upon which so much has been said and written already, it is supplied by the fact that the warnings repeatedly given by those who saw the future clearly (notably by Professor Meldola and Professor Armstrong), have remained largely unheeded. If the conclusions which are forced upon us are unfortunately not of a reassuring nature for our national trade, it is well to remember that nothing is gained by burying our heads in the sand.

The period which we have to consider has been one of extraordinary activity and remarkable development in the coal-tar industry, and before I pass to the economic aspect of the question I will ask you to consider very superficially some of the main points in this advance. In no other industry have such extraordinarily rapid changes and gigantic developments taken place in so short a period—developments in which the scientific elucidation of abstract problems has gone hand in hand with inventive capacity, manufacturing skill, and commercial enterprise. In no other industry has the close and intimate interrelation of science and practice been more clearly demonstrated.

Born in 1858 the colour industry had already attained to a considerable state of development by the year 1886. The period prior to this might well be called the "rosaniline period," since it is chiefly marked by the discovery and development of colouring matters of the rosaniline or triphenylmethane group, such as magenta, aniline blue, Hofmann violet, methyl violet, acid magenta, acid violets, phosphine, Victoria blues, auramine, malachite green, and acid greens. Individual members of other groups had already been discovered, but the latter had not yet attained to the importance which they were destined later to occupy. This is especially the case with the class of colouring matters containing the double-nitrogen radical known as "azo" colours. This group of compounds has, during the fifteen years which we have to consider, attained to such enormous dimensions and importance that this interval may fairly be termed the "azo period." The number of individual compounds belonging to this class which have either been prepared, or are at present preparable, runs into many millions and far exceeds the members of all other groups of colouring matters put to-

gether. In commercial importance also they occupy a position at present far in advance of any other group; the employment of some of them (e.g., the azo blacks), amounting to many thousands of tons annually. A great stimulus to the investigation of the azo compounds was given by the discovery by Böttiger in 1884 of the first colour possessing a direct affinity for cotton (Congo-red), which was followed within a few years by a rapidly increasing series of colours of all shades having similar dyeing properties. The azo colours known prior to this time were either basic colours (aniline yellow, chrysoidine, Bismarck brown, &c.), or acid wool colours (xylydine scarlet, croceine scarlet, &c.). The great simplification of cotton dyeing, brought about by the introduction of the new group of azo colours—"benzo" or "diamine" colours as they were called—led to a rapid increase of their number, and compounds containing two, three, four, or more double-nitrogen groups linking together the residues of various paradiamines (benzidine, tolidine, dianisidine, azoxytoluidine, paraphenylenediamine, naphthylenediamine, &c.), to various naphthol-, amidonaphthol-, and naphthylamine sulphonc acids made their appearance in quick succession. Simultaneously therewith proceeded the discovery and investigation of the various isomeric derivatives of naphthalene required as raw products for the preparation of these colours, an investigation which was largely aided by the classical research on the isomerism of naphthalene compounds carried out in this country by Armstrong and Wynne.

Another method of applying azo colours to cotton, by which much faster shades are obtained, was introduced by Messrs. Read Holiday, of Huddersfield, in 1880, and consisted in producing unsulphonated azo compounds on the fibre by direct combination. Owing to the technical difficulties which were at first encountered in applying this process it has only reached its full development during the last few years at other hands than those of its discoverers. The most important colour produced by this method is paranitraniline red, for which over two hundred tons of chemically pure paranitraniline are manufactured annually.

The search for direct cotton colours led the author in 1887 to the discovery of primuline. This compound having a direct affinity for cotton, and containing at the same time a diazotisable amido group, could be used for the synthesis of various azo colours on the fibre which were remarkable for great fastness to washing. It has had a large employment for the production of fast reds, and the new principle of dyeing which it introduced has been considerably extended in other so-called "diazo" colours. The closer investigation of the thiazol group, to which primuline belongs, further led to the discovery of many other cotton colours belonging to this family, amongst the most important of which are the brilliant greenish-yellow called "turmerine" or "Clayton yellow," the light-fast "chlorophenine" or "chloramine yellow," the pure greenish basic yellow "thioflavine," and the fast cotton-pink "erica."

Passing over the stilbene azo colours and the basic azo ammonium or "Janus" colours, there remains a class of azo compounds to which I must shortly refer, namely, the mordant azo colours, which, with the growing demand for faster shades, have recently come into much prominence. In these compounds the presence of an ortho hydroxyl or carboxyl group gives to the colour the property of combining with metallic mordants, especially chromium oxide, and producing therewith insoluble and fast lakes on the wool or cotton fibre.

We now come to the consideration of three analogously constituted groups of colouring matters, namely, the azines, oxazines, and thiazines. The laborious scientific investigations of Fischer and Hepp, Berntsen, Kehrmann, and others, on the constitution of these groups of compounds, the first members of which (methylene blue, safranin, and Meldola's blue) were discovered in a very early stage of the industry, when little or nothing was

known of their structure, combined with the theoretical views on the quinonoid structure of such colouring matters promulgated by Armstrong, and adopted by Nietzki, has led to the discovery of many valuable new members of these classes. Amongst the latter may be specially mentioned the rosindulines, indoine blue, induline scarlet, rhodulines, &c.

Passing to the pyrone and acridine groups, in which much investigation has also been conducted, the most notable advances have been the discovery of the "rhodamines," a class of pure basic reds, and of the basic yellows and oranges allied to phosphine.

It is in the alizarine group that next to the azo group the greatest progress must be recorded. The demand for fast colours for calico printing and for dyeing chrome-mordanted wool to withstand severe "milling" operations has led to a long series of investigations and patents for producing new derivatives of anthraquinone. These new products, known in commerce as "alizarine Bordeaux," "alizarine cyanines," "anthracene blues," "alizarine viridine," "alizarine saphirol," &c., are polyoxy- or amidoxy-anthraquinones, for the preparation of which either alizarine or nitroanthraquinones are the usual starting points.

Passing over some smaller groups, we now come to a very peculiar class of dye-stuffs containing sulphur, which, although discovered by Croissant and Bretonnière, in 1873, remained confined to a single representative, "Cachou de Laval," until Raymond Vidal, in 1893, obtained a very fast black colouring matter, which dyed unmordanted cotton, by heating para-amidophenol with sulphur and sodium sulphide. The possibility of replacing aniline black in cotton dyeing by a direct colouring matter, and possibly also of obtaining other shades which, though dyed in a single bath, would resist subsequent "cross dyeing" of the wool in mixed fabrics, lent an immense impulse to the study of this class of colouring matters, and although their molecular structure still remains wrapped in obscurity many new representatives have followed each other in rapid succession, ranging in shade from blacks of various hues to browns, olives, greens, and blues. As the most important of these I may mention "Vidal black," "immedial black," "katechine black," "immedial blues," "katechine brown," "katechine green," &c.

It may fairly be claimed, however, that the greatest triumph of the coal-tar industry for the past fifteen years has been the successful production of artificial indigo on a large manufacturing scale.

Returning now from the scientific to the economic aspect of the subject, I will ask you to consider what share we have obtained in the great expansion of trade resulting from all these new discoveries, of which many have originated in this country. The development of the industry in Germany is well illustrated by the following figures:—

Exports from Germany to the World.

	1885.	1895.	1899.
	Tons.	Tons.	Tons.
Aniline oil and salt	1,713	7,135	—
Coal-tar colours (excl. alizarine) .	4,646	15,789	17,639
Alizarine colours	4,284	8,927	—

Again, if we take values, we find that total exports of coal-tar colours from Germany amounted in 1894 to £2,600,000, and in 1898 to £3,500,000, an increase of nearly a million in four years. The latter figure is practically the same as that given by Perkin as an estimate of the world's total production in 1885, showing how great the increase has been since this date.

The value of Germany's entire production is somewhat difficult to arrive at. Witt in his report on the German chemical exhibit at the Paris Exhibition gives as the value of the total chemical industry of Germany for the year 1897 the enormous sum of 46½ million pounds sterling. Of this sum Lefèvre estimates that at least one-tenth may be put down to colouring matters, and another tenth to

raw, intermediate, and synthetic products from coal-tar other than colours, and he thus assigns for the total annual value of the coal-tar industry of Germany the sum of 9 to 10 million pounds sterling. With the increase in the production of synthetic indigo it may be taken to-day to considerably exceed this figure.

One may well wonder what becomes of this enormous quantity of coal-tar products. According to the United States Consular reports the 3½ million pounds worth of coal-tar colours exported by Germany in 1898 were consumed as follows:—

The United States took	£750,000 worth
The United Kingdom took	£730,000 "
Austria and Hungary took	£350,000 "
Italy took	£225,000 "
China took.. .. .	£270,000 "

whilst the rest of the world took the remainder.

The great increase in production in Germany is further shown by the growth in the capital and number of work-people employed. Thus, according to a report of the Badische Works recently issued, the capital of this company, which was increased in 1889 from £900,000 to £1,050,000, will be further augmented this year by the issue of £750,000 worth of debentures. The number of work-people employed by this company in 1900 was 6485, as against 4800 in 1896, an increase of over 33 per cent in four years. The firm of Leopold Cassella and Co., of Mainkur, near Frankfurt, have increased the number of their work-people from 545 in 1890, to 1800 in 1900.

(To be continued).

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.*

By CHARLES BASKERVILLE.

(Concluded from p. 181).

III. Determination of the Atomic Weight of Thorium.

As this is a preliminary paper a detailed discussion of the various atomic weights accorded thorium by the several workers is beyond its scope, and will be reserved for a subsequent communication. Suffice it to say the compounds made use of, as reported by Clarke (*Smithsonian Institution*, "Constants of Nature," Revised 1897, V., 204), viz., the sulphate, oxalate, acetate, and formate, offer little promise of either concordant or satisfactory results. Brauner and Pavlicek (*Chem. Soc. Proc.*, Lond., 1901, xvii., 63) have recently called attention to a serious source of error in using the anhydrous sulphate. The careful work of Brauner (*Chem. Soc. Trans.*, Lond., 1898, lxxiii., 951), on the heptahydrated thorium tetrammonium oxalate gives good results for that substance, but in atomic weight work it is desirable to have as few factors as possible for consideration. It is a matter for surprise that none of the halogen compounds have ever been used. The tetrachloride was selected for this preliminary work. It may be that the bromide will yield even better results.

Preparation of Thorium Tetrachloride.—Thorium dioxide was prepared from the purest insoluble citrate by intense ignition, ground to an impalpable powder in an agate mortar, and an intimate mixture made with a thick paste composed of corn starch and pure sucrose syrup. Balls 5 to 8 m.m. in diameter were made from this, dried, and baked at 140–150° C. in a platinum milk-pan until thoroughly browned. They were then heated in a closed platinum crucible with a Bunsen burner until thoroughly carbonised. About a dozen of these black pellets were placed in a perfectly clean dry combustion tube. Freshly prepared, pure dry chlorine was passed through the tube, that portion immediately surrounding the balls being

* Presented at the Denver Meeting of the American Chemical Society, August 27, 1901.

heated to dull redness. At first a white vapour formed; some settled upon the tube quite a distance from the heat, and some was swept into the lime absorption tower by the chlorine. In Chydenius's paper (*loc. cit.*) it appears that Berzelius observed this "*weißer dampf*," and he states that it is not finely divided thorium chloride. This is the impurity which was noted above. Then beautiful fern-like crystals, only slightly volatile, began to form immediately over and on the balls. These crystals are the purest compound of thorium ever prepared in this laboratory.* After two hours the heat was removed, and the tube allowed to cool in a current of chlorine, which was subsequently removed by pure dry air free from carbon dioxide.

These absorbed water, and were quite soluble. The white volatile vapour mentioned was even more deliquescent. The fernoid crystals were dissolved in water; the solution made up to 100 c.c. in a standard flask, and aliquot portions measured out by means of a calibrated standard burette, whose outlet was so constricted as to deliver $\frac{1}{100}$ c.c. by drops.

Those portions taken for the determination of thorium were measured directly into weighed platinum crucibles, which were placed in perforations of a porcelain plate over a water-bath and evaporated to dryness. The gelatinous oxychloride was gently heated first with a Bunsen burner, and then ignited to a constant weight with the blast-lamp. A beautiful white glistening residue of thorium dioxide was obtained.

For the determination of chlorine, measured quantities were taken, diluted to 75 c.c., acidified with 1 to 2 drops pure nitric acid. Just below the boiling-point the chlorine was precipitated with a weighed quantity of silver nitrate prepared according to Stas. The precipitate was caught in a weighed Gooch crucible, the suction flask being placed in an asphalted box. The crucible and silver chloride were then dried in a dark air-bath at $140-150^{\circ}$ C. to a constant weight. The acid washed asbestos from which the matte was made was previously digested in boiling hydrochloric acid, then water, then hot nitric acid, and finally washed with boiling water until not the faintest evidence of the presence of halogens was obtained.

The following are the results obtained:—

Taken.	Thorium dioxide found.	Per 100 c.c.
A. { 25 c.c.	0.0903	0.3612
	Silver chloride found.	Cl per 100 c.c.
10 c.c.	0.0812	0.2007
	Thorium dioxide found.	Per 100 c.c.
B. { 15 c.c.	0.0542	0.36133
	Silver chloride found.	Cl per 100 c.c.
15 c.c.	0.1220	0.201056

Calculations.

$$\begin{aligned} \text{A. } \frac{XO_2}{Cl_4} &= \frac{0.3612}{0.2007} \therefore X = 223.2 \\ \text{B. } \frac{XO_2}{Cl_4} &= \frac{0.36133}{0.201056} \therefore X = 223.3 \end{aligned} \quad \left. \vphantom{\begin{aligned} \text{A. } \frac{XO_2}{Cl_4} &= \frac{0.3612}{0.2007} \\ \text{B. } \frac{XO_2}{Cl_4} &= \frac{0.36133}{0.201056} \end{aligned}} \right\} \begin{array}{l} \text{Atomic weight} \\ \text{of thorium.} \end{array}$$

It is very interesting here to note that both Hermann's (Clarke's "Constants of Nature, Revised 1897, Part V., 204) and Delafontaine's (*Arch. Sci. Phys. et Nat.*, [2], xviii., 343) results obtained from $2ThSO_4.9H_2O$, and corrected by the observations of Hillebrand (*Bulletin U.S. Geological Survey*, No. 90, 29) to $ThSO_4.4H_2O$, give 223.06 ± 0.3426 . On account of the doubt as to the composition the sulphate and the wide divergence in the value obtained (223.23) from the accepted atomic weight of thorium, Clarke correctly threw it out of consideration.

* I was assisted in the preparation of the tetrachloride and dry ether by Dr. A. S. Wheeler, to whom I wish to express thanks.

From the preliminary values obtained above, which were not reduced to a vacuum, the results assume importance.

As the tetrachloride is so readily decomposed by water, and a direct comparison between a known amount of the tetrachloride and the oxide obtained therefrom is desirable, a complete analysis of the body was made.

Preparation of Pure Anhydrous Ether.—Ether, which had stood over calcium chloride for a year, was decanted over fresh fused calcium chloride, and allowed to remain a week. It was then distilled and placed over freshly cut sodium, and allowed to stand four days. It was again distilled, and placed over fresh sodium, and left three days until no more bubbles of hydrogen escaped. This process was repeated until fresh sheets of sodium showed no tarnishing, and no hydrogen bubbles were observable. It was finally distilled. In all these operations especial precautions were taken to prevent the absorption of a trace of moisture.

More tetrachloride was prepared, and that part of the tube on each side and just above the pellets placed in a perfectly dry Soxhlet apparatus. At the upper end of the reflux condenser was attached a calcium chloride tube. After the apparatus was in place it was learned that the ground glass connection of the condenser was not airtight. A selected velvet cork was substituted. When the extraction had continued about six hours it was discovered that an overlooked small defect of the cork had permitted the gradual introduction of about a drop of water, which came from the sweating of the condenser overhead. As this vitiated the experiment, the ether was evaporated, and the whole dissolved in water. During the evaporation a small amount of hydrochloric acid was detected in the vapour. For that reason the experiment must be discarded, but the results are given:—

$$\begin{array}{l} \text{C. } \left\{ \begin{array}{l} \text{Thorium dioxide found} \dots\dots\dots 0.01020 \\ \text{Chlorine found} \dots\dots\dots 0.05636 \end{array} \right. \end{array}$$

whence—

$$\frac{XO_2}{Cl_4} = \frac{0.0102}{0.05636} \therefore 224.65 \text{ atomic weight.}^*$$

The pellets, which were covered with excrescences of crystals of the tetrachloride, were repeatedly shaken in a small Erlenmeyer flask with about 10 c.c. of pure dry ether. The ether was filtered directly into a weighed platinum crucible, which was placed in a vacuum desiccator in the bottom of which was pure concentrated sulphuric acid, and above chipped paraffin. The tetrachloride appears to be soluble in about 1000 parts of dry ether. Proper precautions were taken to dry the air used to relieve the vacuum of the desiccator and prevent back rush of moist air from the pump. The crucible was dried at 105° C. for half-an-hour in an air-bath already heated, and weighed. The finely crystallised tetrachloride was dissolved in 2 c.c. of pure distilled water to decompose the chloride and form the oxychloride, evaporated to dryness, ignited, and weighed. The following results were obtained:—

Tetrachloride used	0.0822 gm.
Dioxide found	0.0674 "

hence—

$$\frac{XO_2}{XCl_4} = \frac{0.0574}{0.0822} \therefore 222.13 \text{ atomic weight.}$$

In all calculations O = 16, Cl = 35.45, and Ag = 107.93. Another ether extract was made as above, weighed, and dissolved in water, and the chlorine determined by titration with a standard silver nitrate solution, using potassium chromate as indicator—method of Pelouze. Tetrachloride used, 0.01 gm.; c.c. of silver nitrate required, 3.9, each c.c. being equivalent to 0.001 gm. chlorine; hence, 0.0039 gm. chlorine or 39 per cent. The percentage of the oxide obtained from the chloride was 69.83.

* Higher chlorine value decreases atomic weight of thorium.

Calculating for ThCl_4 —

	Using 222.	Using 223'3.	Found.
Th.. ..	61'03	61'18	
or—			
ThO_2 ..	69'82	70'17	69'83
Cl_4 ..	38'97	38'84	39'00 percent

These discrepancies do not deserve discussion, as the data are far too few for ascribing the proper atomic weight to thorium. The last analysis is important, however, as we have secured a substance of known composition, which may be prepared pure, and which lends itself for atomic weight determinations, as the dual constituents, thorium and chlorine, can be estimated with accuracy. The figures hold interest, however, as it may be asserted that the real mass equivalent of thorium is much below that hitherto ascribed to it. It is of greater interest to attribute the old values to a constant unknown impurity in practically all the materials used. This constituent must be an element of much higher atomic weight.

With this evidence of the complexity of thorium the problem now engrossing my personal attention is the separation of the compounds of this element, the proof of their purity and determination of the physical constants and chemical properties. From insufficient data already obtained, in case the element be tetravalent, it appears that the atomic weight lies between 260 and 280. On account of the extensive occurrence in this State (North Carolina) of the monazite sands from which the original material was obtained, if the investigation give a successful issue, I should like to have the element known as *Carolinium*, and have the symbol Cn.

As this is a preliminary paper only, it may not be out of place to state the lines of research bearing immediately upon the subject that are already under way in this laboratory.

1. The preparation of an adequate quantity of perfectly pure thorium compounds with which to continue the study of radio-activity, the spectrum, and to obtain sufficient tetrahalides for the determination of the true atomic weight of that element, which is assuredly different from the number usually accorded it, and dependent at present upon evidence not wholly satisfactory.

2. An investigation of several of the old thorium compounds like the hydrated sulphates, citrates, &c., and determination of their composition.

3. An investigation of the volatile chloride obtained in the preparation of the thorium tetrachloride.

University of North Carolina,
June 1, 1901.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Continued from p. 179).

H. Influence of Nitration with Higher Percentage of Water on the Stability of Gun-cotton.

WHILST experimenting upon the influence exerted by different proportions of the nitration acids on the stability of the product, a diminution in the percentage of nitrogen was found to occur upon prolonged boiling of the product with water. In order to test the practical value of the method given for preparation of gun-cotton with such nitration mixtures, which contain 8 to 11 per cent of water, it had yet to be determined whether these products were less stable towards boiling water than those prepared from the quite concentrated acid mixtures. This

has so far not appeared probable, but a definite statement on this point is desirable in consideration of its practical significance. For this purpose two nitrations were now carried out: the one (A), with the usual acid mixture of three parts concentrated sulphuric acid and one part fuming nitric acid, *i.e.*, H_2SO_4 69'14, HNO_3 23'91, H_2O 6'07, N_2O_4 0'88; the other (B), with a mixture of the following composition:— H_2SO_4 63'64 per cent, HNO_3 25'54 per cent, H_2O 10'82 per cent.

We will call the nitration products obtained A and B. Both bodies were now treated several times with hot and boiling water, and the influence of this treatment on the percentage of nitrogen determined. The following table gives the results obtained.

Treatment received by the nitration products.	Percentage of nitrogen.	
	A.	B.
Washed half-a-day with cold, then one day with hot water.. ..	214'46 c.c. NO 13'45 % N E.P. = 161° $t = 3' 9''$	217'58 c.c. NO 13'64 % N E.P. = 158° $t = 3' 5''$
Washed half-a-day with cold, then three days with hot water.. ..	215'03 c.c. NO 13'48 % N E.P. = 170° $t = 4' 40''$	215'16 c.c. NO 13'49 % N E.P. = 163° $t = 4' 30''$
Half-a-day with cold, then one and a-half days with hot water, and finally boiled for two hours, the water showing no acid reaction.. ..	214'78 c.c. NO 13'47 % N	215'33 c.c. NO 13'50 % N
Do. With five hours' further boiling	213'00 c.c. NO 13'36 % N	214'56 c.c. NO 13'45 % N

Product B, therefore, on treatment with hot and boiling water, behaves similarly to A; the nitrogen diminishes slightly, but remains higher than that in A. Accordingly, the nitration with the acid mixtures containing water used by us yields as stable a product as that with the concentrated acid mixtures used formerly.

I. Behaviour of Different Kinds of Cotton on Nitration, specially with regard to the Preparation of Collodion-Cotton.

According to Nettlefold, wood-cellulose and cotton behave differently on nitration. With the same acid mixture, he obtained from the former a product with 11'2 per cent N and 41'6 per cent soluble matter; from the latter the highest degree of nitration and a solubility of only 8 per cent. In actual practice, wood-cellulose is not often used for the preparation of collodion-cotton, but it is possible that the difference in the proportion of lignin contained by the various kinds of cotton, as well as morphological differences, might play a certain part.

The view is held in some places that different kinds of cotton show a dissimilar behaviour among themselves, and to this is traceable the phenomenon reported, that, with the same acid mixtures, sometimes soluble and then again only difficultly soluble products are obtained.

With the complicated structure of the cellulose molecule and the numerous possible isomers on the one hand, and the deviating morphological structure of the filaments of different kinds of cotton on the other hand, it must be admitted that this statement is *a priori* possibly accurate.

Researches were now instituted with cottons of different properties for spinning purposes, for which we have to thank Messrs. E. Zollinger-Jenny, in Zürich. The nitration mixture always had the composition 63'84 per cent H_2SO_4 , 19'96 per cent HNO_3 , 19'2 per cent H_2O ; the remaining experimental conditions were naturally exactly the same for all the nitrations.

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

Expt.	Sample.	C.c. NO per 1 grm.	N per cent.	Solu- bility.	In- crease.
1.	Chemically pure wadding	187'58	11'76	} Completely soluble.	159
2.	American cotton (middling fair) ..	184'40	11'56		157
3.	American cotton (Florida)	186'21	11'67		153
4.	Egyptian cotton, white (Albassi) ..	186'39	11'69		155
5.	Egyptian cotton, natural	185'16	11'61		154

Hence, from these five samples no essential difference can be inferred. All the nitration products show complete solubility. The products from the four commercial substances differ in the proportion of nitrogen no more than 0.13 per cent N. This difference is no doubt due to difference in purity of the samples.

Accordingly, we do not think the undesirable deviations and results on nitrating cotton can be explained by the use of different materials as the starting-point, but they are more likely due to unlike conditions of nitration; principally to differences in the proportion of water, which have hitherto been overlooked and considered unimportant.

K. Examination of Commercial Varieties of Collodion-cotton ("Soluble" Nitrocellulose) for Explosive Gelatin and Art Silk.

By "collodion-cotton" or "soluble nitrocellulose" is understood products which are used for quite different purposes. In one case, complete solubility in ether-alcohol is of the first importance—to which belongs the material used for surgical and photographic purposes, and, above all, for the Chardonnnet art silk. With others, on the other hand, the object is to get a good "explosive gelatin" with nitro-glycerin (in the proportion of 5 to 7 per cent of the nitrocellulose to 95 to 93 per cent nitro-glycerin); this being the foundation of some of the most important explosives. The products which serve best for both purposes are different from one another. Hitherto no definite publication has appeared as to the properties requisite for each case, and the means by which they may be obtained, but for the first purpose (collodion) a smaller proportion of nitrogen than in the second (explosive gelatin) seems requisite.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall during this month is again below the average; the actual amount measured at Oxford is 1.86 inches, the average for the past thirty-five years is 2.39 inches, showing a deficit of 0.53 inch, which, added to the previous deficit, makes a total of 0.92 inch, or 5.0 per cent on the average.

Our bacteriological examinations of 519 samples have given the results recorded in the following table; we have also examined 44 other samples, from special stand-pipes, wells, &c., making a total of 563 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	215
New River, filtered (mean of 130 samples) ..	7
Thames, unfiltered (mean of 25 samples) ..	873
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 277 samples)	19
Ditto ditto highest	141
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	266
River Lea, from the East London Company's clear-water wells (mean of 37 samples) ..	17

Of the 444 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 32 samples, or 7.4 per cent, were sterile. Not one sample contained as many as 150 microbes, while only eight samples, or 1.8 per cent, contained more than 100 microbes per c.c., thus showing the remarkable purity of the London supply during the past month. The mean number of microbes in the eight excess samples was 118, against a corresponding mean of 212 in six excess samples during August.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

RADIUM.

By W. MARCKWALD.

THE interesting communications of P. and S. Curie, also of Giesel and others, on the production of strongly radioactive bodies from the barium salts arising from pitch-blende, have been hitherto lacking in a more exact description of the method of crystallisation used by the authors. But it may without difficulty be concluded from these publications that radium and barium salts form isomorphous mixtures; for otherwise, on re-crystallisation of a barium chloride containing but little radium salt, pure barium salt would separate from the solution, until the proportion of the salt corresponded to the mixture, but to increase the proportion of radium salt in the mixture by crystallisation would be impossible.

From researches which I carried out with barium chloride from the mixed chlorides, similar in quality to that used by P. and S. Curie as their starting-point, I found this opinion confirmed. Starting with only 100 grms. of this product a strongly active preparation of radium was obtained, and the crystallisation was conducted on the lines of fractional distillation, which is necessary in the case of isomorphous mixtures. For this purpose the salt is left in the water, and allowed to crystallise partially. The first crystallised fraction is richer, relatively, in radium salt than the original material. With continued crystallisation the radio-

activity of the separating product diminishes regularly, until, finally, the salt remaining in solution is scarcely active at all. The first crystallised portion is now dissolved in hot water, separated by crystallisation on cooling from the mother-liquor, which is used for re-crystallising the second portion, and so on. In this way about 90 grms. absolutely inactive barium salt was finally separated off, while the remaining 10 grms. was divided into about 12 fractions of varying degrees of radio-activity.

The best fractions exhibited clearly the interesting properties observed by the above mentioned authors. The anhydrous salt is strongly phosphorescent; the one containing water of crystallisation weakly so, but more strongly radio-active; glass was coloured by it deep brown in a few days. The action upon the barium platino-cyanide screen was successfully demonstrated to a large audience, and the action upon the electroscope can be recognised at a distance of 5 d.m.

THE CHEMISTRY OF DEPOSITS IN STEAM BOILERS.*

By W. E. RIDENOUR.

THIS is a very old subject, having been worked upon by many eminent chemists on both sides of the Atlantic, and from many different views.

Some have devoted their ideas to the prevention of scale formation inside the boiler, under which heading you will find in literature and on the market at the present time as many remedies as there are patent medicines for the ailments of the human body.

Others have taken up the purification of water outside the boiler; while again, others have debated as to the chemical salts existing in these deposits. With this latter subject I wish to deal, in conjunction with a study of their physical appearance.

Before proceeding with these deposits, I wish to call attention to the vast amount that accumulates in a boiler from a good water for steam purposes in a month's run.

An average of several analyses of a water which is largely used in Philadelphia, the Schuylkill, is as follows (when it is clear):—

	Grains per U.S. gallon.
Organic and volatile	5.060
Calcium sulphate	3.560
Magnesium sulphate	0.602
Sodium chloride	1.167
Calcium carbonate	0.357
Solids	10.746

There are 4.519 grains of scale-forming matter per gallon in this water, which, for a 1000 horse-power plant, the average for these times, and allowing 4 gallons to be evaporated per hour per horse-power, will give the following:—

4 gallons per hour per horse-power.
10 hours per day.

40 gallons per day per horse-power.
26 days per month.

1040 gallons per month per horse-power.
1000 horse-power.

1,040,000 gallons per month per 1000 horse-power.
4.519 grains per gallon of scale-forming matter.
4,699,760 grains.

671 pounds of sediment per month.

The above are small figures for the average plant, as private wells are generally used, which are much worse, ranging from 25 to 75 grains per gallon; in one case in particular I recall from the soft coal district of this State, it amounted to 83 grains per gallon, and so situated that it had to be used.

Small wonder, then, that so many workers have been attracted to this troublesome subject.

For convenience, I have divided these accumulations into four classes, according to the predominating constituent:—

1. The calcium sulphate scales.
2. The calcium carbonate scales.
3. The silicate scales.
4. The magnesia scales.

The calcium scales are, as a class, very hard and porcelain-like (examples Nos. 7 and 9), but a few are quite soft (example No. 8). They can generally be told from the others with the aid of a simple magnifier, by their glassy or vitreous appearance.

There has been some debate as to how the calcium sulphate exists, whether as a hydrate or an anhydrite.

Prof. V. B. Lewes (CHEMICAL NEWS, 1889, vol. lix., p. 222) states that it is first deposited as a hydrate, $(\text{CaSO}_4)_2\text{H}_2\text{O}$, by coming in contact with the heated plates forms the anhydrite CaSO_4 . I have always found it to occur as the anhydrite CaSO_4 (example No. 7, from South Australia):—

	Per cent.
Moisture at 100° C.	0.23
Calcium sulphate	94.89
Magnesium hydrate	1.98
Silica	0.25
Organic and undetermined	2.65

The calcium carbonate deposits are usually moderately soft, but the presence of even small quantities of either magnesia, calcium sulphate, or silica modifies them to variable degrees of hardness, some equalling those of the first class.

Example of soft scale, No. 10.

Example of hard scale, No. 11.

If moderately pure, they are readily recognised by the magnifier, being composed of distinct crystals (samples Nos. 10 and 15); some being easily seen by the naked eye (samples Nos. 12 and 14). This crystalline appearance is pronounced in some deposits of but 50 per cent calcium carbonate, sample No. 14, which contains—

	Per cent.
Calcium carbonate	51.73
Calcium sulphate	26.10
Magnesium hydrate	11.32
Silica	0.42
Iron oxide and alumina	0.39
Organic and undetermined	10.04

The silicate scales, to me, are the most strange and interesting. They are most common in the Southern States, but I have received a few from different States.

In these scales there is a combination of calcium oxide and silica, existing as calcium silicate, which, I think, is formed during the violent boiling under pressure in the boiler, by the free silicic acid occurring in the water reacting with the calcium carbonate.

Sample No. 2 from Louisiana:—

	Per cent.	Calcium silicate.
Calcium carbonate	36.40	
Calcium oxide	7.32	7.32
Silica	41.00	7.84
Magnesium hydrate	0.50	
Alumina	9.68	15.16
Organic and undetermined	5.10	

* Read before the Chemical Section of the Franklin Institute, March 28, 1901. From the *Journal of the Franklin Institute*, clii., No. 2.

Sample No. 3, from New Jersey:—

	Per cent.	Calcium silicate.
Moisture at 100° C.	4'55	
Calcium carbonate	7'47	
Magnesium hydrate	2'74	
Calcium oxide	21'94	21'54
Silica	51'07	23'50
		45'04
Calcium sulphate	1'56	
Iron oxide	1'34	
Organic and undetermined ..	9'33	

An extreme case is sample No. 4, from Olympia, Washington:—

	Per cent.	Calcium silicate.
Calcium oxide	36'42	36'42
Silica	40'51	39'02
		75'44
Magnesium hydrate	3'04	
Iron oxide and alumina	2'66	
Oil	11'50	
Organic and undetermined ..	5'87	

Sample No. 16, from this State, is especially interesting, as I was able also to get a sample of the water. The scale contained:—

	Per cent.	Calcium silicate.
Calcium oxide	5'42	5'42
Silica	48'02	5'80
		11'22
Calcium sulphate	3'95	
Magnesium hydrate	3'58	
Iron oxide and alumina	27'08	
Organic and undetermined ..	11'95	

The water analysed:—

	Grains per U.S. gallon.
Calcium carbonate	1'311
Calcium sulphate	0'104
Magnesium carbonate	1'147
Sodium chloride	0'850
Silica	1'469
Organic and volatile	1'340
Solids	6'221

In comparing these two analyses, it is seen that the calcium carbonate occurring naturally in the water has completely disappeared before forming into scale, making quite possible the hypothesis that the silica has reacted with the calcium carbonate during evaporation.

The silicate scales have no characteristic physical appearance.

The magnesia scales have caused considerable disagreement among the many investigators as to which salt of magnesium is found in these deposits, whether magnesium oxide, magnesium hydrate, or magnesium carbonate. Magnesium hydrate is now the generally accepted combination, and I agree that this is the usual salt occurring.

Sample No. 5, from Texa, contained:—

	Per cent.
Calcium carbonate	4'25
Calcium sulphate	7'50
Magnesium hydrate	82'95
Silica	3'10
Iron oxide and alumina	1'18
Organic and undetermined ..	1'02

But a few specimens have been examined by me which contained magnesium carbonate.

Sample No. 17, from Pennsylvania:—

	Per cent.
Calcium oxide	4'39
Magnesia	59'79
Carbonic acid	22'29
Silica	5'36
Alumina	2'92
Organic and undetermined ..	5'25

which is equivalent to—

Calcium carbonate	7'83
Magnesia	38'23
Magnesium carb., (Mg.CO ₃) ₄ Mg.(OH) ₂ ..	42'25
Silica	5'36
Alumina	2'92
Organic and undetermined ..	3'41

It is quite possible that magnesium carbonate is first deposited from the water upon being heated, but changes after forming into scale, in proportion to the heat to which it is exposed, into magnesium hydrate, or even magnesium oxide.

There are no marked characteristics under the glass to distinguish these deposits from the others.

It is not safe to express an opinion of a water supply by an analysis of the usual sample of deposit taken from a steam boiler, as exclusive of the influence on the scale of the various preventives used, different portions of the same boiler form scales of quite different composition.

Samples Nos. 12 and 13 are from the same boiler, but are as different as if formed by a carbonate and a sulphate water.

Sample No. 12 contains 96 per cent of calcium carbonate, while No. 13 has 76 per cent of calcium sulphate.

This can be explained if we consider the location in the boiler from which the two samples were taken.

Scale No. 12, composed chiefly of calcium carbonate, came from near the feed-pipe, where the water first comes in contact with the heat, thereby driving off the free carbonic acid and precipitating the calcium carbonate thus held in solution; while the calcium sulphate still remains dissolved until it reaches the hottest part of the boiler, the bottom plate, where sample No. 13 collected. Prof. V. B. Lewes mentions that he examined several scales from different parts of the same boiler, all of which varied considerably.

THE MEASUREMENT OF GOLD AND SILVER BUTTONS IN QUANTITATIVE BLOWPIPE ASSAYS.*

By JOSEPH W. RICHARDS.

(Concluded from p. 183).

Note on the Quantitative Gold or Silver Assay.—The writer makes the fusion on charcoal in preference to a Freiberg carbon crucible, which is often unobtainable. When finished, it is always possible to make the slag quite liquid and then to pour out the lead *in toto*, leaving only clean slag on the charcoal. At first it will be best to pour out on a cold steel anvil or plate, whence the lead may be picked up and placed at once on the cupel for scorifying. The writer has frequently poured the lead directly from the charcoal on the previously heated cupel, and then commenced immediately to scorify, sometimes without even allowing the lead to set. This will usually succeed for one with a steady hand, and several minutes can thus be saved.

In scorifying, if the blowpipe-tip is advanced almost to the nearer edge of the flame, an oxidising flame of great power without a well-defined point is obtained, before which the lead oxidises with great rapidity. 1800 m.grms. of lead were thus scorified to 300 m.grms. in two minutes;

* *Journal of the American Chemical Society*, xxiii., No. 4.

and, in general, one-half to two-thirds of the time usually consumed in scorification can be saved.

For fine cupellation, it is not absolutely necessary to pre-heat the cupel. The button is placed on the freshly-struck cupel, a spot under the button strongly heated, on which the button drops as it melts. Then the cupel is turned slowly, keeping the button half-way up the far side, and the flame always heating the cupel just under it, which is thus dried before the button comes on to it.

By using such devices as the above to save time, the gold or silver assay may often be run through in from ten to fifteen minutes, with an extra five minutes for separately determining gold and silver, if necessary.

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
rooths m.m.	M.grm.	M.grm.	Cu. m.m.
2.	0'0001	0'00004	0'000004
3.	0'0003	0'00015	0'000014
4.	0'0006	0'00035	0'000034
5.	0'0013	0'00069	0'000065
6.	0'0022	0'0012	0'00011
7.	0'0035	0'0019	0'00018
8.	0'0052	0'0028	0'00027
9.	0'0074	0'0040	0'00038
10.	0'0101	0'0055	0'00052
11.	0'0134	0'0073	0'00070
12.	0'0174	0'0095	0'00091
13.	0'0222	0'0121	0'00115
14.	0'0277	0'0151	0'00144
15.	0'0340	0'0185	0'00177
16.	0'0413	0'0225	0'00214
17.	0'0495	0'0269	0'00257
18.	0'0588	0'0320	0'00305
19.	0'0692	0'0376	0'00359
20.	0'0807	0'0439	0'00419
21.	0'0934	0'0508	0'00485
22.	0'107	0'0584	0'00558
23.	0'123	0'0667	0'00637
24.	0'139	0'0758	0'00724
25.	0'158	0'0857	0'00818
26.	0'177	0'0963	0'00920
27.	0'199	0'108	0'0103
28.	0'221	0'120	0'0115
29.	0'246	0'134	0'0128
30.	0'272	0'148	0'0141
31.	0'300	0'163	0'0156
32.	0'330	0'180	0'0172
33.	0'362	0'197	0'0188
34.	0'396	0'216	0'0206
35.	0'432	0'235	0'0225
36.	0'470	0'256	0'0244
37.	0'511	0'278	0'0265
38.	0'553	0'301	0'0287
39.	0'598	0'325	0'0311
40.	0'645	0'351	0'0335
41.	0'695	0'378	0'0361
42.	0'747	0'406	0'0388
43.	0'802	0'436	0'0416
44.	0'859	0'467	0'0446
45.	0'919	0'500	0'0477
46.	0'982	0'534	0'0510
47.	1'047	0'569	0'0544
48.	1'115	0'606	0'0579
49.	1'186	0'645	0'0616
50.	1'261	0'686	0'0655
51.	1'338	0'727	0'0695
52.	1'418	0'771	0'0736
53.	1'501	0'816	0'0780
54.	1'588	0'863	0'0824
55.	1'678	0'912	0'0871
56.	1'771	0'963	0'0920
57.	1'867	1'016	0'0970
58.	1'967	1'070	0'1022
59.	2'07	1'126	0'1075
60.	2'18	1'185	0'1131
61.	2'29	1'245	0'1189

Number on the scale.	Weight of gold button.	Weight of silver button.	Volume of the button.
rooths m.m.	M.grm.	M.grm.	Cu. m.m.
62.	2'40	1'307	0'1248
63.	2'52	1'371	0'1309
64.	2'64	1'438	0'1373
65.	2'77	1'506	0'1438
66.	2'90	1'577	0'1505
67.	3'03	1'649	0'1575
68.	3'17	1'724	0'1646
69.	3'31	1'802	0'1720
70.	3'46	1'881	0'1796
71.	3'61	1'963	0'1874
72.	3'76	2'047	0'1954
73.	3'92	2'133	0'2037
74.	4'09	2'222	0'2122
75.	4'25	2'313	0'2209
76.	4'43	2'407	0'2298
77.	4'60	2'504	0'2390
78.	4'78	2'602	0'2485
79.	4'97	2'704	0'2582
80.	5'16	2'81	0'268
81.	5'36	2'91	0'278
82.	5'56	3'02	0'289
83.	5'77	3'14	0'299
84.	5'98	3'25	0'310
85.	6'19	3'37	0'322
86.	6'41	3'49	0'333
87.	6'64	3'61	0'345
88.	6'87	3'74	0'357
89.	7'11	3'87	0'369
90.	7'35	4'00	0'382
91.	7'60	4'13	0'395
92.	7'85	4'27	0'408
93.	8'11	4'41	0'421
94.	8'38	4'55	0'435
95.	8'65	4'70	0'449
96.	8'92	4'85	0'463
97.	9'20	5'00	0'478
98.	9'49	5'16	0'493
99.	9'78	5'32	0'508
100.	10'08	5'48	0'524

Specific Gravity of Gold-silver Alloys.

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
0	19'258	51	13'488
1	19'099	52	13'409
2	18'940	53	13'331
3	18'785	54	13'254
4	18'632	55	13'178
5	18'483	56	13'103
6	18'335	57	13'029
7	18'190	58	12'955
8	18'047	59	12'882
9	17'906	60	12'811
10	17'767	61	12'739
11	17'631	62	12'669
12	17'497	63	12'600
13	17'364	64	12'531
14	17'234	65	12'463
15	17'106	66	12'395
16	16'979	67	12'329
17	16'855	68	12'263
18	16'731	69	12'198
19	16'610	70	12'133
20	16'491	71	12'069
21	16'374	72	12'007
22	16'258	73	11'944
23	16'144	74	11'882
24	16'031	75	11'821
25	15'920	76	11'761
26	15'810	77	11'700
27	15'702	78	11'641
28	15'595	79	11'582
29	15'490	80	11'525

Silver. Per cent.	Specific gravity.	Silver. Per cent.	Specific gravity.
30	15.386	81	11.467
31	15.283	82	11.410
32	15.183	83	11.353
33	15.083	84	11.297
34	14.984	85	11.242
35	14.887	86	11.187
36	14.791	87	11.133
37	14.697	88	11.079
38	14.603	89	11.026
39	14.511	90	10.973
40	14.420	91	10.921
41	14.330	92	10.871
42	14.241	93	10.819
43	14.153	94	10.768
44	14.066	95	10.718
45	13.980	96	10.668
46	13.896	97	10.619
47	13.813	98	10.570
48	13.730	99	10.521
49	13.648	100	10.473
50	13.568		

ON THE CÆSIUM-ANTIMONIOUS FLUORIDES AND SOME OTHER DOUBLE HALIDES OF ANTIMONY.

By H. L. WELLS and F. J. METZGER.

WE have made a thorough study of the double salts formed by cæsium fluoride and antimonious fluoride, with the result that five compounds have been prepared. This is an unusual number for a series of double salts, and it gives a good illustration of the facility with which cæsium forms such compounds.

The salts to be described have the following formulæ:—

Type.	
1:3	CsF·3SbF ₃
1:2	CsF·2SbF ₃
4:7	4CsF·7SbF ₃
1:1	CsF·SbF ₃
2:1	2CsF·SbF ₃

The previously described antimonious double fluorides, all of which were prepared by Flückiger (*Pogg. Ann.*, 1852, lxxxvii., 245), are as follows:—

Type.	
1:1	KF·SbF ₃
2:1	2KF·SbF ₃ , 2LiF·SbF ₃ , 2NH ₄ F·SbF ₃ .
3:1	2NaF·SbF ₃

The following chlorides, bromides, and iodides have been described:—

Type.	
1:2	RbCl·2SbCl ₃ . (Wheeler, <i>Amer. Journ. Sci.</i> , [3], xlv., 269).
3:4	3NH ₄ I·4SbI ₃ ·9H ₂ O. (Schäffer, <i>Pogg. Ann.</i> , cix., 611).
1:1	NH ₄ Cl·SbCl ₃ . (Deherain, <i>C. R.</i> , lii., 734). NH ₄ I·SbI ₃ ·2H ₂ O. (Nicklès, <i>C. R.</i> , li., 1097). KI·SbI ₃ ·H ₂ O. " " RbCl·SbCl ₃ . (Remsen and Saunders, <i>Am. Chem. Journ.</i> , xiv., 152). 3:2 3KI·2SbI ₃ ·3H ₂ O. (Schäffer, <i>loc. cit.</i>). 3NaI·2SbI ₃ ·12H ₂ O. " " 3NH ₄ I·2SbI ₃ ·3H ₂ O. " " 3RbCl·2SbCl ₃ . (Wheeler, <i>loc. cit.</i>). 3RbBr·2SbBr ₃ . " " 3RbI·2SbI ₃ . " " 3CsCl·2SbCl ₃ . (Setterberg, <i>Öfversigt K. Vetensk. Akad. Förhandl.</i> , 1882, 23; Remsen and Saunders, <i>loc. cit.</i>).

2:1	2NH ₄ Cl·SbCl ₃ . (Deherain, <i>loc. cit.</i>). 2NH ₄ Cl·SbCl ₃ ·H ₂ O. (Poggiale, <i>C. R.</i> , xx., 1180). 2KCl·SbCl ₃ . (Jacqueline; Poggiale, <i>loc. cit.</i> ; Benedict, <i>Proc. Am. Acad.</i> , xxix., 212). 2KCl·SbCl ₃ ·2H ₂ O. (Benedict, <i>loc. cit.</i>).
7:3*	7RbCl·3SbCl ₃ . (Remsen and Saunders, <i>loc. cit.</i>). 7RbBr·3SbBr ₃ . (Wheeler, <i>loc. cit.</i>). 7KCl·3SbCl ₃ . (Herty, <i>Am. Chem. Journ.</i> , xv., 81). 7KBr·3SbBr ₃ ·8H ₂ O. (Herty, <i>loc. cit.</i>).
3:1	3NH ₄ Cl·SbCl ₃ ·1½H ₂ O. (Poggiale, <i>loc. cit.</i>). [3KCl·SbCl ₃]. (Poggiale, <i>loc. cit.</i>). It is probable, according to Herty, <i>loc. cit.</i> , that 3KCl·SbCl ₃ does not exist). 3NaCl·SbCl ₃ . (Poggiale, <i>loc. cit.</i>).
4:1	4NH ₄ I·SbI ₃ ·3H ₂ O. (Schäffer, <i>loc. cit.</i>).

Upon comparing the cæsium double fluorides with the salts already known, it is to be noticed that two types of the former, 1:3 and 4:7, do not occur among the latter, and that the 3:4, 3:2, 7:3, 3:1, and 4:1 types were not found among the cæsium-antimonious fluorides. The absence of a 3:2 fluoride is remarkable, since the salt 3CsCl·2SbCl₃ is very sparingly soluble, and because this is a very prominent type among the chlorides, bromides, and iodides. It is evident that a close relation does not exist between the cæsium-antimonious fluorides and the other antimonious double halides, and that the types of the former could not have been predicted from a consideration of the latter. In range, the cæsium double fluorides extend farther at the antimony end than the others, while they do not extend as far at the alkali-metal end of the series of types.

When all the types of antimonious double halides are considered, they are remarkable for their large number, ten. This number is probably greater than is the case with any other negative element. The types, 1:3, 1:2, 4:7, 3:4, 1:1, 3:2, 2:1, 7:3, 3:1, and 4:1, with two or three exceptions, are the simplest that can exist in such number between the two extremes, and arithmetically they extend almost as far in one direction as the other.

Method of Preparation.—Solutions of cæsium fluoride and antimonious fluoride were prepared by treating cæsium carbonate and antimonious oxide, each with an excess of pure hydrofluoric acid. To the antimonious solution the cæsium salt was gradually added in small quantities, and after each addition the liquid was evaporated and cooled until crystallisation took place. If a homogeneous product was obtained a portion was removed for analysis, and the process was continued until finally the liquid contained a very large excess of cæsium fluoride. In every case the products were carefully inspected to make sure that they were not mixtures, and at least two crops of a salt were always prepared under somewhat different conditions, and were shown by analysis to be identical in composition before they were accepted as true compounds.

Method of Analysis.—The crystals were carefully dried by pressing between filter-papers, and the portions to be analysed were preserved in glass weighing tubes which were coated within with a very thin layer of paraffin. For the determination of antimony and cæsium a portion was heated in a platinum crucible with concentrated sulphuric acid until all the hydrofluoric acid was removed, the residue was dissolved in hydrochloric acid, antimony was precipitated as sulphide, collected on a Gooch crucible, and weighed after drying in a small oven containing carbon dioxide. Cæsium was weighed as normal sulphate. Fluorine was determined by converting it into silicon fluoride, collecting the latter in water, and titrating with sodium hydroxide, according to a modification of Offermann's method. The results of these fluorine determinations were invariably somewhat too low, as we found by testing the method with pure potassium silicon fluoride; hence, the chief value of these deter.

* This type was described as 23:10; see Wells and Foote (*Amer. Journ. Sci.*, iii., 461).

minations consists in showing that the salts under investigation were not oxy-compounds.

1:2 Cæsium-Antimonious Fluoride, $\text{CsF} \cdot 2\text{SbF}_3$.—This salt was obtained in the form of beautiful, transparent needles by adding 2 or 3 grms. of cæsium fluoride to a solution of about 50 grms. of antimonious fluoride in somewhat dilute hydrofluoric acid solution, heating to boiling, and cooling. Two separate crops gave the following results upon analysis:—

	Calculated for CsSb_2F_7 .	Found.	
		I.	II.
Cæsium	26.28	26.44	—
Antimony	47.43	47.36	47.42
Fluorine	26.28	25.23	—

1:3 Cæsium-Antimonious Fluoride, $\text{CsF} \cdot 3\text{SbF}_3$.—This salt crystallises in the form of stout, transparent prisms. It was obtained by evaporating the mother-liquors from the preceding compound, and cooling, or by the use of somewhat less cæsium fluoride in proportion to the antimonious fluoride in a more concentrated solution. Two crops gave the following results:—

	Calculated for $\text{CsSb}_3\text{F}_{10}$.	Found.	
		I.	II.
Cæsium	19.47	17.81	17.60
Antimony	52.71	52.95	53.89
Fluorine	27.82	27.01	26.84

The rather wide variation of the results from the calculated quantities is probably due to the fact that the crystals were taken from a very concentrated antimonious fluoride solution, and were consequently not quite pure, even after careful drying on paper.

4:7 Cæsium-Antimonious Fluoride, $4\text{CsF} \cdot 7\text{SbF}_3$.—This salt crystallises in transparent plates, and is formed in the presence of a little larger proportion of cæsium fluoride than the preceding compounds. It was obtained, for instance, upon adding about 4 grms. of cæsium fluoride to a mother-liquor from the last salt, and crystallising by cooling. Two crops gave the following results:—

	Calculated for $\text{Cs}_4\text{Sb}_7\text{F}_{26}$.	Found.	
		I.	II.
Cæsium	28.80	28.99	—
Antimony	45.47	46.02	46.03
Fluorine	25.73	24.58	24.61

We cannot say that we are absolutely sure about the formula of this apparently complicated double salt. It cannot be a 1:2 compound, for not only is it entirely distinct in appearance from $\text{CsF} \cdot 2\text{SbF}_3$, but coming as it does from a strong antimony solution, the results would naturally come too high rather than too low for antimony. The results vary too widely from a 2:3 ratio to make that probable, but they approach somewhat more closely the 3:5 ratio. The following calculations will show that we have selected the most probable formula:—

Calculated for $\text{Cs}_3\text{Sb}_5\text{F}_{11}$.	Calculated for $\text{Cs}_5\text{Sb}_7\text{F}_{18}$.	Calculated for CsSb_2F_7 .
31.86	29.75	26.28
43.11	44.75	47.43
25.03	25.50	26.28

1:1 Cæsium-Antimonious Fluoride, $\text{CsF} \cdot \text{SbF}_3$.—In the presence of still greater proportions of cæsium fluoride this salt is produced by cooling the properly concentrated solution. It forms square prisms, the ends of which are not usually modified by any planes. Three crops gave the following analysis:—

	Calculated for CsSbF_4 .	Found.		
		I.	II.	III.
Cæsium	40.43	41.44	41.19	—
Antimony	36.47	35.85	35.66	35.52
Fluorine	23.10	22.30	—	—

2:1 Cæsium-Antimonious Fluoride, $2\text{CsF} \cdot \text{SbF}_3$.—This salt is formed under a wide range of conditions when

cæsium fluoride is present in large excess in comparison with the antimonious fluoride. It crystallises in apparently rhombic prisms, which are often somewhat flattened. Four crops, made under very different conditions, gave the following results:—

	Calculated for Cs_2SbF_6 .	Found.			
		I.	II.	III.	IV.
Cæsium	55.30	54.81	—	—	—
Antimony	24.95	24.72	24.59	24.92	24.64
Fluorine	19.75	19.42	—	—	—

By the use of very concentrated cæsium fluoride solutions with comparatively small amounts of antimonious fluoride, no evidence was obtained of the existence of any double salt containing more cæsium fluoride than the one just described.

Cæsium-Antimonious Iodide, $3\text{CsI} \cdot 2\text{SbI}_3$.—It appears that no compound of cæsium iodide with antimonious iodide has been described. The sparingly soluble chloride, $3\text{CsCl} \cdot 2\text{SbCl}_3$, is well known, and this was the only double chloride that Remsen and Saunders (*Amer. Chem. Journ.*, xiv., 152) were able to prepare, although four rubidium-antimonious chlorides are known. It is evident that the slight solubility of cæsium-antimonious chloride makes it impossible to prepare concentrated solutions of the component chlorides, and consequently prevents the formation of salts of other types. We have found that an iodide which corresponds in composition to the chloride can be readily prepared. It is sparingly soluble in hydriodic acid solutions, and it exists in two distinct forms, one of which is brick-red, and apparently octahedral in form, while the other is yellow, and occurs in thin hexagonal plates. The octahedral salt was prepared by mixing antimonious iodide and cæsium iodide in rather strong hydriodic acid solutions, while the yellow hexagonal salt was made in much less strongly acid solutions, particularly upon diluting them with water, boiling, and cooling. Two crops of each form were analysed as follows:—

	Calculated for $\text{Cs}_3\text{Sb}_2\text{I}_9$.	Found.			
		Red salt.		Yellow salt.	
		I.	II.	I.	II.
Cæsium	22.39	23.46	—	22.15	—
Antimony	13.47	13.91	13.19	14.36	14.52
Iodine	64.14	62.98	—	63.03	—

This was the only double iodide that we were able to obtain.

There is little doubt that a corresponding bromide exists, for we observed, while engaged in work with another object in view, that a yellow precipitate is produced when the bromides of cæsium and trivalent antimony are brought together in solution. Having overlooked the fact that the compound had not been described, we neglected to analyse the product.

Cæsium-Antimonic Halides.—So little is known concerning the double halides of quinquevalent elements that it seemed desirable to study the cæsium-antimonic compounds. Setterberg (*Ofversigt K. Vetensk. Akad. Förhandl.*, 1882, 23) has described a single double chloride, $\text{CsCl} \cdot \text{SbCl}_5$, and we have confirmed his result, but by using widely varying conditions we have been unable to prepare any other compound. Setterberg's salt crystallises in long, colourless, transparent needles. A crop of it gave the following results upon analysis:—

	Calculated for CsSbCl_6 .	Found.
Cæsium	28.54	29.14
Antimony	25.75	26.43
Chlorine	45.71	43.94

We have extended our investigation to antimonic fluoride and cæsium fluoride, but the results were disappointing from the fact that we were able to prepare but one double salt, while Marignac (*Leibig's Ann.*, cxlv., 237) has described two potassium antimonic fluorides. Either cæsium in this case unexpectedly fails to show as

great a tendency to form double salts as does potassium, or else we have failed to find the proper conditions for producing them.

The salt obtained by us apparently contains hydroxyl, although prepared in strong hydrofluoric acid solutions, and has the formula $\text{CsF} \cdot \text{SbF}_4\text{OH}$. It crystallises on cooling warm, rather concentrated solutions in the form of bundles of transparent needles. Two crops gave the following analyses:—

	Calculated for CsSbF_6OH .	Found.	
		I.	II.
Cæsium . . .	36.44	37.77	—
Antimony . . .	32.87	31.82	31.72
Fluorine . . .	26.03	25.54	26.18
Hydroxyl . . .	4.66	[4.87]	—

—*American Journal of Science*, vol. xi., No. 66.

NOTICES OF BOOKS.

The Periodic Classification and the Problem of Chemical Evolution. By GEORGE RUDORF, B.Sc., University College, London. London and New York: Whittaker and Co. 1900.

In attempting to condense a *résumé* of the above subjects into a small text-book of a couple of hundred pages, the author has set himself an important and difficult task. The necessity for such condensation unfortunately lies at the door of our present examinational system; for it is manifestly impossible for the average student, in addition to his many other duties, so to study the original literature involved in the above subjects as to make himself master of all the speculations and theories that have been advanced.

Provided the book is used as a convenient means of bringing before the notice of students a brief outline of the various theories with a view to more complete studies of the original literature, well and good; but if the book is to be used as a sort of concentrated essence to meet the requirements of the Board of Examiners, the matter assumes a more serious aspect, for then it is necessary that the author himself should be a thorough master of the many researches and speculations he seeks to condense, or otherwise there is a danger that both master and pupil "shall fall into the ditch."

That this is no imaginary danger is seen by a cursory examination. For instance, in Sir Norman Lockyer's notes printed on the first page, he says:—"If you well consider J. J. Thomson's work in connection with the dissociation hypothesis, you will find its importance to be that he negatives the old suggestions which you reproduce."

And in the chapter dealing with the question of rare earths there are some very hasty assertions and serious errors, that point to great haste, if not carelessness, on the part of the author. It is stated, on page 146, that Welsbach succeeded in decomposing didymium by fractionally crystallising the double nitrates of "old didymium" with ammonium nitrate; no mention being made of the part played by lanthanum, upon the presence of which depends the whole success of the method. On page 148, the hypothetical bodies, Z_α , Z_β , and Z_γ , of M. Lecoq de Boisbaudran are referred to as having been distinguished by their spark spectra; while, in point of fact, they have their origin in a different kind of spectra altogether, called by de Boisbaudran "reversion spectra." On the same page we are told that Sir William Crookes has separated old yttria into some bodies that he has named, "and are known as, samarium, mosandrum, yttrium, and yttrium- α ." It is scarcely necessary to point out that Sir William Crookes is not responsible for any of the above-named elements; and certainly he has never suggested that they form the component parts of old yttria.

Errors and hasty conclusions of this kind, instilled into the mind of a student at the commencement of his scientific career, cannot fail to do harm, and the subjects will have to be re-learned, re-digested later on.

We are sorry to have to point out these faults, because many things in the book will be found of considerable value to the student. We can only hope that he may be able to separate the good from the bad; and, after all, that is what has to be done in the case of most books. It is well printed and indexed.

MEETINGS FOR THE WEEK.

FRIDAY, 25th.—Physical, 5. "On the Variation with Temperature of the Thermo-electromotive Force and of the Electric Resistance of Nickel, Iron, and Copper, between the Temperatures of -200° and $+1050^\circ$," by E. P. Harrison. "On Asymmetry of the Zeeman Effect," by G. W. Walker.

BIRKBECK INSTITUTION,

Breams Buildings, Chancery Lane, E.C.

Next Session commences September 30th.

DAY and EVENING CLASSES in SCIENCE.—CHEMISTRY, PHYSICS, GEOLOGY, METALLURGY, and ASSAYING. With Practical work in highly-equipped LABORATORIES.

Preparation for all the Examinations in Science for the University of London, Conjoint Board, and Pharmaceutical Society.

A Complete Course of Study in Theoretical and Practical METALLURGY and MINING.

Prospectus free. Calendar 6d. (post 8d.) on application.

THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION.

Directors:

The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., F.R.S.

Superintendent of the Laboratory:

Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

The Laboratory is open free of charge to Workers of either sex, and any nationality, prosecuting individual investigations; and the extensive collection of Physico-Chemical Apparatus presented by the Founder is available for their use, together with such materials, chemicals, electricity, &c., as the Directors may authorise.

Assistants and a trained mechanic are attached to the Laboratory to aid Workers in the prosecution of their researches.

All persons desiring to be admitted as Workers must send evidence of scientific training, qualification, and previous experience in original research, along with a statement of the nature of the investigation they propose to undertake.

MICHAELMAS TERM.—Monday, October 7, to Saturday, December 14.

LENT TERM.—Monday, January 6, to Saturday, March 22.

EASTER TERM.—Monday, April 14, to Saturday, July 26.

Forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

HANDBOOK OF PATENT LAW.

BY

W. P. THOMPSON, C.E., F.C.S., &c.

The above well known work has just been thoroughly revised, and the large number of alterations made since 1896 in Continental and Foreign Patent Laws have been summarised in an Addendum. Price complete, 2s. 6d.

W. P. THOMPSON & CO., Patent Agents,
6, Lord Street, Liverpool; 322, High Holborn, London, W.C.

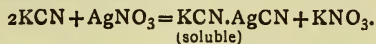
THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2187.

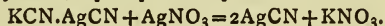
ESTIMATION OF CYANIDE IN THE PRESENCE OF A CHLORIDE.

By FRANK B. GATEHOUSE.

WHEN a solution of AgNO_3 is added to a solution of KCN in the presence of KCl no precipitate is formed whilst any KCN remains in solution:—



But as soon as the silver solution has been added in quantity, more than sufficient for the formation of the double cyanide, a precipitate is produced:—



One molecule of AgNO_3 is therefore required for the first reaction, and an equal amount to form the precipitate of AgCN .

Working on the above facts I have found the following volumetric process for estimating KCN in the presence of KCl or NaCl both expeditious and accurate:—

Measure out a definite amount of the solution containing the cyanide and chloride. Run into it from a burette a decinormal solution of AgNO_3 , until a permanent turbidity appears. At this stage of the process each c.c. of AgNO_3 solution which has been used will correspond to 0.013036 grm. of KCN. Note the reading of the burette, and run into the solution the same volume of silver solution as was required to form the permanent precipitate, and again note the reading. From this point the AgNO_3 added is used in precipitating the chloride. Then add a few drops of K_2CrO_4 solution free from chloride, and judging the end of the reaction by the appearance of the dark red silver chromate, estimate the chloride in the usual manner.

Merchant Venturers' Technical College,
Bristol, October 16, 1901.

THE RELATIVE PROGRESS OF THE COAL-TAR INDUSTRY IN ENGLAND AND GERMANY DURING THE PAST FIFTEEN YEARS.*

By ARTHUR C. GREEN, F.I.C., F.C.S.,
Consulting Chemist and Chemical Engineer.

(Concluded from p. 187).

PASSING now to England, we find that the imports of coal-tar colours into the country are steadily rising, as is shown by the following figures taken from the Board of Trade returns:—

Imports of Coal-tar Dyestuffs into England during the last Fifteen Years (excluding Indigo).

1886	£509,750	1894	£599,000
1887	542,000	1895	710,000
1888	569,000	1896	739,300
1889	609,200	1897	695,400
1890	594,400	1898	739,000
1891	586,300	1899	708,800
1892	542,200	1900	720,000
1893	504,000		

Contrasted with this, the exports of coal-tar colours manufactured in England have fallen from £530,000 in 1890 to £366,500 in 1899. Comparing these figures with the rapidly increasing export trade of Germany, it is seen that, whereas formerly the English export trade in artificial colours was about one-quarter that of Germany, it does not now amount to a tenth part. It is therefore apparent that we have had but little share in the great increase which this industry has experienced during the past fifteen years, and that we have not even been able to supply the expansion in our own requirements. In order to ascertain what proportion of our own needs we at present furnish, I am able to lay before you the following interesting figures, which have been kindly supplied me by the Bradford Dyers' Association and the British Cotton and Wool Dyers' Association, who together form a very large proportion of the entire dyeing trade:—

Colouring-matters Used by Bradford Dyers' Association.

English ..	10 per cent	Swiss ..	6 per cent
German ..	80 „	French ..	4 „

Colouring-matters Used by British Cotton and Wool Dyers' Association.

Aniline colours	{ English .. 22 per cent
	{ Foreign .. 78 „
Alizarine colours	{ English .. 1.65 „
	{ Foreign .. 98.35 „

The English Sewing Cotton Company have also very kindly supplied me with a detailed analysis of their consumption, from which it appears that out of a total of 60 tons of colouring-matters and other dyeing materials derived from coal-tar only 9 per cent were of English manufacture.

The accompanying table of statistics of the six largest German firms gives a fair picture of the present dimensions of the industry in that country. (See next page).

The joint capital of these six firms amounts to at least 2½ millions; they employ between them about 500 chemists, 350 engineers and other technologists, 1360 business managers, clerks, travellers, &c., and over 18,000 work-people. Compared with such figures as these, the English colour manufacture assumes insignificant proportions. The total capital invested in the coal-tar colour trade in England probably does not exceed £500,000, the total number of chemists employed cannot be more than 30 or 40, and the number of workmen engaged in the manufacture does not amount to over a thousand.

A similar relative proportion is maintained in the number of patents for new colouring-matters and other coal-tar products taken by the English and German firms, as is shown by the following table:—

Comparison of Number of Completed English Patents for Coal-tar Products taken during 1886—1900 by Six Largest English and Six Largest German Firms.

German firms—

Badische Aniline Works	179
Meister, Lucius, and Brünig	231
Farbfabriken Bayer and Co.	306
Berlin Aniline Co.	119
L. Cassella and Co.	75
Farbwerk Mühlheim Leonhardt and Co. ..	38

Total of six German firms .. 948

English firms—

Brook, Simpson, and Spiller	7
Clayton Aniline Co.	21
Levinstein	19
Read Holliday and Co.	28
Claus and Reë	9
W. G. Thompson	2

Total of six English firms .. 86

* Read before the British Association (Section B), Glasgow Meeting, 1901.

Position of the Six Largest Colour Works in Germany in the Year 1900.

	Badische Aniline Works.	Meister, Lucius, and Brüning.	Farbenfabriken Bayer and Co.	Berlin Aniline Co.	Cassella and Co.	Farbwerk Mühlheim Leonhardt, and Co.	Total of six firms. About—
Capital.. .. .	£1,050,000	£833,000	£882,000	£441,000	Private concern	£157,000	£2,500,000
Number of chemists.. ..	148	120	145	55	60	450	500
Number of engineers, dyers, and other technologists..	75	36	175	31			350
Commercial staff.. ..	305	211	500	150			1360
Work-people.. .. .	6485	3555	4200	1800	1800		18,260

Dividends (per Cent)—

1897.. .. .	24	26	18	12½	Not known	9
1898.. .. .	24	26	18	15	"	3
1899.. .. .	24	26	18	15	"	5
1900.. .. .	24	20	18	?	"	Nil

Nor does the potential loss which we have sustained by our inability to take advantage of a growing industry represent the sum total of our losses. The new colouring matters, made chiefly in Germany, have in many cases been introduced as substitutes for natural products, which were staple articles of English commerce. Madder and cochineal have been replaced by alizarine and azo-scarlets, the employment of many dye-woods has greatly decreased, whilst at the present moment logwood and indigo are seriously threatened. Regarding the indigo question, so much has been written that I do not propose to occupy space in its further discussion, but will only point out that the complete capture of the indigo market by the synthetic product, which would mean a loss to our Indian dependencies of £3,000,000 a year, is regarded by the Badische Company as so absolutely certain, that having already invested nearly a million pounds in the enterprise, they are at present issuing £750,000 of new debenture capital to provide funds to extend their plant for this purpose. In the last annual report of the Company they say:—

"As regards plant indigo, the directors are prepared and determined to meet this competition in all its possible variations in value. Much strange matter has been published in India as to improvements in the cultivation and preparation of natural indigo, but the illusions of the planters and indigo dealers are destined to be dispelled before facts, which although they are not known to them, will make themselves more felt the larger the production of artificial indigo becomes."

Again, besides the loss of material wealth which the neglect of the coal-tar trade has involved to the country, there is yet another aspect of the question which is even of more importance than the commercial one. There can be no question that the growth in Germany of a highly scientific industry of large and far-reaching proportion, has had an enormous effect in encouraging and stimulating scientific culture and scientific research in *all* branches of knowledge. It has reacted with beneficial effect upon the universities, and has tended to promote scientific thought throughout the land. By its demonstration of the practical importance of purely theoretical conceptions it has had a far-reaching effect on the intellectual life of the nation. How much such a scientific revival is wanted in our own country, the social and economic history of the past ten years abundantly testifies. For in the struggle for existence between nations the battle is no longer to the strong in arm, but to those who are strongest in knowledge to turn the resources of nature to best account.

The position with which we are confronted is in truth a lamentable one, and the way out is not so easy to find. In 1836 it could perhaps still be maintained that we held the key to the situation if we chose to make use of it; inasmuch as the principal raw products of the colour manufacture (tar oils, naphthalene, anthracene, soda, ammonia, iron, &c.), were in great measure imported from England. In a speech to the Academy of Sciences of Munich, in 1878, Professor von Bayer had said:—

"Germany, which in comparison with England and France possesses such great disadvantages in reference to natural resources, has succeeded by means of her intellectual activity in wresting from both countries a source of national wealth. Germany has no longer to pay any tribute to foreign nations, but is now receiving such tribute from them, and the primary source from which this wealth originates has its home, not in Germany, but in England. It is one of the most singular phenomena in the domain of industrial chemistry that the chief industrial nation, and the most practical people in the world, has been beaten in the endeavour to turn to profitable account the coal-tar which it possesses. We must not, however, rest upon our oars, for we may be sure that England, which at present looks on quietly while we purchase her tar and convert it into colours, selling them to foreign nations at high prices, will unhesitatingly cut off the source of supply as soon as all technical difficulties have been surmounted by the exertions of German manufacturers."

Professor von Bayer could not believe that the English manufacturer and capitalist would stand by and see an important industry which had had its origin and early development in his own country taken from him without a strong effort to retain it. Yet the initial advantages which our natural resources afforded us have been neglected, and now, in 1901, the conditions are completely changed. The adaptation of condensing plant to the Westphalian coke ovens has rendered Germany, though still a large buyer from England, no longer dependent on English tar and ammonia; by the development of the ammonia-soda process she no longer requires English alkali; whilst all other raw products of the colour industry can now be purchased in the commercial centres of Germany at least as cheaply as in England, and some even at lower prices. Through the shortsightedness, ignorance, and want of enterprise of those with whom rested the care of the colour industry of this country in its earlier days, the opportunity has been allowed to pass for ever. The English capitalist passed over as not sufficiently profitable for his consideration an industry which at present amounts to 9 or 10 millions sterling annually, and from which his German *confrère* now reaps a dividend of nearly 20 per cent. The English manufacturer considered that a knowledge of the benzol market was of far greater importance than a knowledge of the benzol theory, and after the early but brilliant days in the infancy of the industry, when guided by such eminent workers as Hofmann, Perkin, and Nicholson, commercial progress and scientific investigation went hand in hand, but little encouragement was given here to chemical investigators and discoverers. The control of the industry unfortunately soon passed into the hands of men who had no knowledge and absolutely no appreciation of the science upon which their business rested, and concerned only with getting the ultimate amount of present profit, discouraged all scientific investigations as waste of time and money. The chemist who devoted himself to the elucidation of the

chemical constitution of a colouring matter was regarded by them as an unpractical theorist of no value to a manufacturing business. Even when he discovered new colouring matters of commercial value they were so blind to their own interests and so incapable of believing that any practical good could come out of such theoretical work that in many cases they refused to patent or in any way take advantage of the discoveries made by him.

During recent years this attitude has certainly undergone considerable modification, and some attempt has been made to call in the aid of the science so long neglected. Certain firms indeed must be given the credit of endeavouring to pursue a more enlightened policy, but these attempts have always been directed too much in the expectation of realising immediate financial results. The difficulties which must be encountered in an attempt to regain the lost ground are of necessity very great and quite unappreciated by our business men. It seems, in fact, to have been the opinion of the public and of the average financial man that this industry ought to be easily won back by us by the establishment of a few technical schools, the engagement of a dozen chemists, and the investment of a few thousand pounds in new plant, forgetting that the supremacy of our German competitors has been won by years of patient toil, by the work of hundreds of trained chemists, and by the outlay of millions of capital. Who can be surprised, therefore, if such expectations have not been realised, and if in spite of some notable successes the general position of the colour trade in England to-day presents a gloomy aspect. During years of stagnation in this country the German manufacturers have been realising large profits, a portion of which they have employed in consolidating their businesses, writing off the value of their buildings and plant, and setting aside enormous reserves (the reserve of the Badische Company is over a million pounds); they have gathered round them perfectly working organisations comprising enormous staffs of scientifically and practically trained research chemists, factory chemists with highly specialised knowledge, chemical engineers, dyers, and others; their travellers and agents are in every part of the globe; by long manufacturing experience and unremitting endeavour to improve their processes and plant, they have brought the yields and quality of their products to such a state of perfection that even when the manufacture of these products is no longer covered by patents, they are able to produce them at a cost price which is impossible to any one commencing their manufacture. They have hedged themselves about with a perfect stockade of many hundreds of patents; have accumulated in their laboratories thousands of intermediate products ready at any time to be subjected to any new treatment or combination which research or theory may suggest as likely to yield new results. By the complete range of colours which they are able to offer in each group of dye-stuffs, whether basic colours, acid colours for wool, fast colours dyeing on metallic mordants, diazotisable colours, or direct colours for cotton, and by the invaluable aid and assistance which they can give the dyer in his daily work, they are enabled to retain his custom, even if it sometimes happens that a better and a cheaper article is offered him by the home producer.

Where then are we to look for an improvement? Some would find a remedy in the imposition of heavy protective tariffs, but such tariffs in France have not availed to prevent a similar state of things there, and protection in colouring matters might have a very detrimental effect upon the textile industries of the country. Others expect salvation from the extension of technical schools, but laudable as is the aim of these institutions I cannot see how they can effect much until their raw material is of a very different character to what it is at present, and until the public can be completely disabused of the fallacy that a year or two of technical training pumped into an ignorant schoolboy will produce a better works-chemist than a university course of scientific study laid upon the foundation of a good general education. Others again base their

hopes for the future upon a reform of the patent laws, and seek to compel all patented processes to be worked in this country. Although I am inclined to believe that a portion of our present troubles have been brought about by a bad patent law, framed mainly from an engineering and not from a chemical point of view, and which seems specially designed to foster foreign trade at our own expense, yet I cannot attribute to this cause a too preponderating influence, and am doubtful whether its removal now would materially improve the position. The remedy for the present state of affairs must of necessity be a slow one, and in my opinion can only be found in a better appreciation of the value of science throughout the length and breadth of the land. Until our Government and public men can be brought to realise the importance of fostering the study of science, and of encouraging all scientific industries, until our schools and universities appreciate the importance of a scientific education, until the rewards for public service in science are made equal to those in other branches of the public service, so long will science continue to be held in insufficient esteem in our country. It is not so much the education of our chemists which is at fault as the scientific education of the public as a whole.

When our capitalists more completely realise the importance of calling in the aid of the best scientific skill available, when our universities and technical schools are able to supply a sufficient number of highly educated chemists equal in knowledge, originality, and resource to those trained in German Universities, when our professors and manufacturers are willing to work together in this and other matters, when our patent laws are rendered just to ourselves, we may confidently hope that our natural engineering skill and practical resource will once more bring us to the front.

THE SOLUBILITY OF PHOSPHATIC MANURES IN SOME ORGANIC ACIDS.

By WALTER F. SUTHERST, Ph.D.

THE present-day method of valuing phosphatic manures—that is, the neutral and basic ones—by treating them with a dilute solution of citric acid, or, as recommended by Wagner, an acid solution of ammonium citrate, must naturally leave open the question whether such reagents really represent the dissolving-power of the roots of plants or the acids present in the soil. It was this question which led me to try the action of a few organic acids, viz., acetic, tartaric, and citric, on four typical manures, viz., coprolite (Christmas Island), basic slag, basic superphosphate, and precipitated phosphate.

The samples on analysis were found to contain the following:—

	Per cent P_2O_5 .	Per cent $Ca_3(PO_4)_2$.
Coprolite	39·67	equal to 84·29
Basic slag	13·31	„ 29·13
Basic superphosphate ..	13·01	„ 28·38
Precipitated phosphate ..	37·03	„ 80·73

The method was as follows:—One gram. of the manure was placed in a 100 c.c. graduated flask, and, in the case in using citric acid, 1 gram. of the pure crystallised acid added and the solution made up to the mark with distilled water. In using the remaining two acids, an amount equal to 1 gram. of citric acid (in the form of normal solutions) was added, so that the total acidity of each solution used was exactly the same. The acid was allowed to act on the phosphate for twenty-four hours, with frequent agitation; then the liquid was filtered through a dry filter-paper, and in 50 c.c. of the filtrate the phosphoric acid was estimated. The portion measured off for the estimation of the phosphoric acid was first made alkaline with ammonia; then acid with dilute nitric acid; then an excess of ammonium molybdate solution added; the solution heated on the water-bath three hours,

allowed to cool and settle. The precipitate was washed with dilute ammonium nitrate solution, and then dissolved in dilute ammonia, from which solution the phosphoric acid was again precipitated by magnesia mixture in the usual way.

I. With Acetic Acid were dissolved out from—

	Grm. Mg ₂ P ₂ O ₇ .	Per cent Ca ₃ (PO ₄) ₂ .
a. Coprolite	gave 0.0400	equal to 10.13
b. Basic slag	" 0.0442	" 12.30
c. Basic superphosphate	" 0.0666	" 18.53
d. Precipitated phosphate	" 0.1572	" 43.72

II. With Tartaric Acid—

a. Coprolite	gave 0.1174	equal to 32.60
b. Basic slag	" 0.0570	" 15.85
c. Basic superphosphate	" 0.1020	" 28.37
d. Precipitated phosphate	" 0.2808	" 78.12

III. With Citric Acid—

a. Coprolite	gave 0.0618	equal to 17.17
b. Basic slag	" 0.0707	" 19.67
c. Basic superphosphate	" 0.0891	" 24.79
d. Precipitated phosphate	" 0.2562	" 71.27

On calculating the ratio of dissolved tricalcic phosphate to the total amount present I get the following figures:—

Manure.	Acetic acid. Per cent.	Tartaric acid. Per cent.	Citric acid. Per cent.
Coprolite	12.01	43.41	20.36
Basic slag	42.22	54.41	67.50
Basic superphosphate ..	65.29	87.38	99.26
Precipitated phosphate .	54.15	96.76	88.28

The large difference in the solubilities of the coprolite and basic slag compared with the basic superphosphate and precipitated phosphate is readily explained by the fact that minerals and bodies exposed to a high temperature or fused are much more difficult to dissolve than the same compound when recently precipitated—an instance which one comes across frequently in the laboratory.

Basic superphosphate, invented by Mr. J. Hughes, really belongs to the class of precipitated phosphates, though from its method of preparation—by adding lime to ordinary superphosphate—the reaction which takes place must be a "dry precipitation."

Though citric acid seems to be now fixed upon as the reagent in testing phosphates, it is not at all a true representative, as may be gathered from the above results, for the most satisfactory results as a general solvent are given by tartaric acid.

The Agricultural College,
Holmes Chapel.

CONTRIBUTIONS TO THE SCIENCE OF THE NITROCELLULOSES.*

By G. LUNGE and J. BEBIE.

(Concluded from p. 190).

WE have pointed out already that, by observing certain conditions, products completely soluble in ether-alcohol with up to 13 per cent nitrogen may be obtained, which is a higher percentage than that necessary for explosive gelatin. As regards solubility, the relation of a nitrocellulose to ether-alcohol will not be identical with that to nitro-glycerin as solvent, but there should be an analogy between the two cases.

In order to investigate this question we have examined specimens of collodion cotton used in commerce for both purposes before mentioned, viz., (A) of that used for explosive gelatin, and (B) of that manufactured for art silk in Spreitenbach, near Zürich.

Specimen A yielded, per 1 grm., 196.70 c.c. NO = 12.33 per cent N; solubility in ether-alcohol, 95.49 per cent; explosion-point, 198.5°, after warming for 4' 46".

Specimen B gave an explosion-point of 197°, after heating for 4' 45"; therefore, differing immaterially from specimen A. This is the less important that a specimen of highly nitrated gun-cotton from the army factory in Thun, destined for military purposes, is almost identical as regards explosiveness with the less highly nitrated collodion-cotton, as the following figures show. (The experiments were carried out simultaneously in the same apparatus, and hence under the same conditions):—

Collodion-cotton A. (Brig).	Gun-cotton C. (Thun).
E.P. = 197°	E.P. = 195°
t = 4' 8"	t = 4' 4"
N = 12.33 per cent	N = 13.25 per cent

In other experiments also, we found a somewhat higher explosion-point for collodion-cotton than for well washed gun-cotton. Badly washed products naturally have too low an explosion-point.

In this case little was to be gathered from the stability test, as is seen by the following:—

Specimen.	Beginning of reaction in Abel test.
C. Gun-cotton (Thun)	15' 17'
A. Collodion-cotton (Brig) ..	No colouration after two hours
B. Collodion-cotton (Spreitenbach)	20' 24'
Temperature of the water-bath = 80°.	

L. The Behaviour of Nitrocelluloses in Polarised Light.

The behaviour of the cotton filaments in polarised light is altered by nitration. Its characteristic iridescence with predominating yellow and brownish-yellow illumination is lost. The nitrated filament still shows feeble double refraction, the highly nitrated have a blue iridescence, while no pronounced colour was to be observed in the others. This gives us an excellent means of qualitative examination for unattacked cellulose.

Attempts have already been made to differentiate the various degrees of nitration according to their behaviour in polarised light. According to Morton-Liebschütz, hexa-nitrocellulose should be recognised by the great brightness of the filaments and their grey colour, the penta-nitrocellulose by their blue, and the tetra-nitrocellulose by their yellow colour.

With regard to hexa- and penta-nitrocellulose, we will leave out the observations made by Lunge and Weintraub, as they coincide with ours. Among the numerous products lying between penta- and hexa-nitrocellulose (C₁₂...) which were examined with this view, a mixture of grey and blue illuminated filaments were certainly observable in polarised light. Those in particular were blue in one certain position, and those perpendicular to them, or nearly so; on turning the platform the filaments formerly grey became blue, and *vice versa*. The grey colour, therefore, cannot be looked upon as a characteristic of any particular degree of nitration.

We did not observe the violet shade between the highly nitrated celluloses and the group of the collodion-cottons mentioned by Chardonnet. From about 198 c.c. NO downwards most of the products showed a grey light, which passes into a soft yellow tone on blending with the top light, and remaining unchanged in many cases. According to Chardonnet, with 160—180 c.c. NO, the colour of the threads changes from straw-yellow to orange. Our products between 170 and 180 c.c. NO were similar to those mentioned above; nothing definite can be said of those under 160 c.c.; in these the structure was more or less destroyed. As the behaviour in polarised light is not only dependent on the chemical composition, but is also a function of the physical properties, conclusive observations were impossible in these cases.

The observation with the polarisation microscope

* Zeitschrift für Angewandte Chemie, 1901, Heft 20.

serves, therefore, where the structure of the filaments is not destroyed (i.e., with nitration with concentrated acid mixtures) to distinguish unchanged cellulose by the iridescency from the highly nitrated products (from decanitrocellulose upwards) by the blue illumination; but further distinctions are not possible, and with more dilute acid mixtures (used for collodion cotton), by which the structure may be lost, the recognition of the unchanged cellulose and of the different degrees of the nitration is not possible.

M. Coloration of the Nitrocelluloses with Iodine.

The different behaviour towards iodine and sulphuric acid gives a ready means of distinguishing cellulose amongst nitrocellulose. Cellulose assumes a deep blue colour, while nitrocellulose shows the brown colour of the iodine solution, and, after washing the latter, it becomes again white. But their behaviour is different with iodine solution alone, without previous treatment with sulphuric acid. With the true gun-cottons no lasting colouration was to be observed; on the other hand, with the less highly nitrated celluloses, it appeared that the brown colour remained after washing, and increased as the degree of nitration diminished. But this difference of coloration is not sufficiently pronounced to form a foundation for an accurate determination of the degree of nitration.

SOME ABRIDGMENTS IN CHEMICAL CALCULATIONS.*

By Prof. JOSEPH W. RICHARDS.

IN calculating the volumes of gases produced from any weight of solid, liquid, or gaseous substance, a few simple relations render the calculations very direct.

The molecular formula of a gas represents in an equation one volume, relatively, of that gas. The molecular weight represents, likewise, a relative weight. If, now, we call the total relative weights entering into a given reaction kilograms., then each molecule of gas represented in the equation will represent the volume of molecular weight in kilos. of a gas, which, by Avogadro's law, is the same for all gases. For hydrogen this volume is—

$$\frac{2}{0.09} = 22.22 \text{ cubic metres,}$$

and this is the volume of molecular weight in kilos. of all gases. We can therefore say that, calling the relative weights entering into an equation kilograms., each molecule of gas in the equation represents 22.22 cubic metres of that gas.

By similar reasoning and calculation we can affirm the relations between the relative weights considered as grms., pounds, or ounces, and the actual volumes thus represented in litres, cubic feet, or cubic inches. We therefore have the following relations:—

If relative weights be—	Each molecule of gas is—
Kilos.	22.22 cubic metres.
Grms.	22.22 litres.
Pounds	355.9 cubic feet.
Ounces	22.24 cubic feet.

(Volumes being at 0° C. and 760 m.m.).

E.g., in the manufacture of acetylene gas—

Molecules of gas = relative volumes . . . I
 $\text{CaC}_2 + \text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{CaO}$
 Relative weights 64 + 18 = 26 + 56

Whence it follows that—

64 kilos. of CaC_2 + 18 kilos. of H_2O produce 22.22 cubic metres of C_2H_2 .

64 grms. of CaC_2 + 18 grms. of H_2O produce 22.22 litres of C_2H_2 .

64 pounds of CaC_2 + 18 pounds of H_2O produce 355.9 cubic feet of C_2H_2 .

64 ounces of CaC_2 + 18 ounces of H_2O produce 22.24 cubic feet of C_2H_2 .

The most complicated of chemical equations bear the application of these simple principles in a similar manner.

To calculate quickly from the volume composition of a gas the weight of carbon, hydrogen, or oxygen which it will contain in unit of volume, we need only to apply the following principles:—

Equal volumes of all gases contain equal numbers of molecules; therefore, if a gas molecule of any gas whatever contains one atom of carbon, or of hydrogen, or of oxygen, we can say of such gases that equal volumes of them contain equal numbers of atoms of carbon, hydrogen, or oxygen, as the case may be, and therefore equal weights of each of those elements respectively.

But 1 cubic metre of CO contains 0.54 kilo. of carbon; therefore, that statement is true of 1 cubic metre of any other gas with one atom of carbon in its molecule, such as CO_2 , CH_4 , &c. Gases with two atoms of carbon in their molecule, as C_2H_6 , would contain $2 \times 0.54 = 1.08$ kilos. of carbon by the same principles, and so on to C_3H_8 , &c. Carbonic oxide, CO, also contains 0.72 kilo. of oxygen per cubic metre; whence a similar set of relations for CO_2 , &c. Hydrogen gas, H_2 , contains 0.09 kilo. of hydrogen per cubic metre, whence it follows that 1 cubic metre of a gas with one atom of hydrogen in its molecule, as HCl, will contain—

$$\frac{0.09}{2} = 0.045 \text{ kilo.}$$

of hydrogen.

We can therefore state that, for a gas containing in its molecular formula one atom of carbon, hydrogen, or oxygen, the weights of those elements present in a given unit of volumes would be—

	Carbon.	Hydrogen.	Oxygen.
In 1 cubic metre	0.54 kilo.	0.045 kilo.	0.72 kilo.
„ 1 litre . .	0.54 grm.	0.045 grm.	0.72 grm.
„ 1 cubic foot .	0.54 oz.	0.045 oz.	0.72 oz.
„ 1 „ „ .	0.0337 lb.	0.00281 lb.	0.045 lb.

For a gas with two atoms of carbon, hydrogen, or oxygen in its molecule, the respective weights are twice the above; and so on for any gas, no matter how complicated. For practical calculations, I recommend keeping only the above constants in mind, and simply doubling or trebling the volume of the gas, instead of doubling or tripling the constant.

E.g.: Calculate the weight of carbon, hydrogen, and oxygen present in 1 cubic metre and 1 cubic foot of natural gas of the following composition:—

	Per cent.	(By volume).
CO_2	5.7	= 0.057
C_2H_4	0.9	= 0.009
CO	15.4	= 0.154
H_4	8.3	= 0.083
CH_2	3.8	= 0.038
N_2	65.9	= 0.659
	100.0	1.000

Calculation for Carbon.

CO_2	= 0.057
C_2H_4	$0.009 \times 2 = 0.018$
CO	= 0.154
CH_4	= 0.038
	$0.267 \times 0.54 = 0.1442$ kilo. per cubic metre.
	$0.267 \times 0.0337 = 0.0090$ pound per cubic foot.

* Read before the Chemical Section of the Franklin Institute, March 28, 1901. From the *Journal of the Franklin Institute*, clii., No. 2.

Calculation for Hydragen.

C₂H₄ 0.009 × 4 = 0.036H₂ 0.083 × 2 = 0.166CH₄ 0.038 × 4 = 0.1520.354 × 0.045 = 0.01593 kilo. per
cubic metre.0.354 × 0.00281 = 0.0010 pound
per cubic foot.

Calculation for Oxygen.

CO₂ 0.057 × 2 = 0.114

CO = 0.154

0.268 × 0.72 = 0.1930 kilo. per
cubic metre.0.268 × 0.045 = 0.01206 pound
per cubic foot.

These principles save much labour, especially in metal
lurgical calculations.

ESTIMATION OF HYDRATE IN THE PRESENCE
OF ALKALI CARBONATE.*

By W. E. RIDENOUR.

AFTER reviewing the several methods of estimating caustic
alkali in the presence of carbonate, and carbonate in the
presence of hydrate, the method proposed by R. T.
Thompson appeared to be the best, if accurate.

Mr. Thompson ("Sutton's Volumetric Analysis," fifth
edition) weighs off a quantity of the sample to be tested,
dissolves in water, and titrates with standard acid, using
phenolphthalein, which gives the hydrate and half of the
carbonate; then, by adding methyl-orange and continuing
the titration, the other half of the carbonate can be found.

To test the above method, a solution of sodium carbonate
C.P. was made and titrated, with following
results:—

Sodium carbonate solution.	Normal hydrochloric acid.	Indicator.
10 C.C.	9.535	Methyl-orange.
	4.574	Phenolphthalein.
10 C.C.	4.985	Methyl-orange.
	9.149	Phenolphthalein.
20 C.C.	9.971	Methyl-orange.
	Decinormal hydrochloric acid.	
10 C.C.	94.78	Methyl-orange.
	45.026	Phenolphthalein.
10 C.C.	49.858	Methyl-orange.

Standard acid, with the factor 1.6377, was used, the
sodium carbonate solution was well diluted, and the end of
the burette kept below the surface of the liquid.

The indicators (U.S.P., 1890) were also tested; four
drops in 100 c.c. of distilled water responded at once to
one drop of normal acid and alkali.

A solution of sodium hydrate, C.P., was then made and
tested in the same manner.

Sodium hydrate solution.	Normal hydrochloric acid.	Indicator.
10 C.C.	11.822	Methyl-orange.
10 C.C.	11.565	Phenolphthalein.
	0.257	Methyl-orange.
10 C.C.	11.565	Phenolphthalein.
	Decinormal hydrochloric acid.	
10 C.C.	2.67	Methyl-orange.
	115.444	Phenolphthalein.

* Read before the Chemical Section of the Franklin Institute,
March 28, 1901. From the *Journal of the Franklin Institute*, clii.,
No. 2.

The above would seem to indicate the presence of car-
bonate in the hydrate, so barium chloride solution (W.
Smith, *Journ. Soc. Chem. Ind.*, i., 85) was added to 100
c.c. of sodium hydrate solution in a flask until it ceased to
give a precipitate (produced only a slight cloudiness),
water added to make 200 c.c., allowed to settle, and the
clear liquor titrated.

Clear sodium hydrate solution.	Decinormal hydrochloric acid.	Indicator.
20 C.C.	2.57	Methyl-orange.
	115.464	Phenolphthalein.

If carbonate was present then it is impossible to
eliminate the same by precipitation with barium chloride
solution.

Combining sodium carbonate and sodium hydrate solu-
tions in various proportions, the following results by titra-
tion were obtained:—

Sodium hydrate solution.	Sodium carbonate solution.	Normal hydrochloric acid.	Indicator.
10 C.C.	10 C.C.	16.088	Phenolphthalein.
		5.191	Methyl-orange.
10 C.C.	10 C.C.	21.2706	Methyl-orange.
10 C.C.	1 C.C.	11.9762	Phenolphthalein.
		0.7196	Methyl-orange.
10 C.C.	3 C.C.	12.9528	Phenolphthalein.
		1.6962	Methyl-orange.

	Decinormal hydrochloric acid.	
1 C.C.	1 C.C.	15.98
		5.60
		Phenolphthalein.
		Methyl-orange.

NOTE.—Allowance must be made, in proving these re-
sults by the factor 104.5726, for the possible pre-
sence of carbonate in the sodium hydrate used.

By comparing the different results, it can be seen that
phenolphthalein does not indicate half of the carbonate,
either alone or in combination with hydrate, but a definite
ratio is observed between the results in the titration of
pure sodium carbonate when using methyl-orange alone
and using phenolphthalein followed by methyl-orange.

Multiply by 2 the number of cubic centimetres of normal
hydrochloric acid necessary to neutralise a definite quan-
tity of pure sodium carbonate indicated by methyl-orange,
using phenolphthalein, then methyl-orange, and divide by
the number of cubic centimetres of normal hydrochloric
acid necessary to neutralise the same quantity of pure
sodium carbonate, using methyl-orange only, gives
104.5726, i.e.,—

$$\frac{2 \times 4.985}{9.535} = 104.5726.$$

For figures, see Table I.

Therefore, to obtain the number of cubic centimetres of
normal acid corresponding to the carbonate present in a
mixture of alkaline hydrate and carbonate, multiply by 2
the number of cubic centimetres of normal acid indicated
by methyl-orange, using phenolphthalein, then methyl-
orange, and divide by the factor 104.5726.

Nitromannite and Nitrocellulose.—Léo Vignon and
F. Gerin.—One of the authors has already shown that
cellulose, when submitted to several degrees of nitration,
in all cases gives nitrated derivatives which energetically
reduce a cupro-potassic solution. The authors now under-
take the examination of the nitrated derivatives of man-
nite, and examine to find whether the nitric ethers of this
alcohol of relatively simple constitution are susceptible
of acquiring reducing properties after nitration. Their
researches lead them to the following conclusions:—(a) Penta-
and hexa-nitromannite energetically reduce cupro-
potassic solution; (b) this property is not attributable to
the formation of mannose; (c) nitromannite, treated with
ferrous chloride, gives no reduction with mannite. With
regard to this property, it does not behave like the nitro-
celluloses.—*Comptes Rendus*. cxxxiii., No. 14.

ON A SYSTEM OF INDEXING CHEMICAL
LITERATURE;

ADOPTED BY THE CLASSIFICATION
DIVISION OF THE U.S. PATENT OFFICE.*

By EDWIN A. HILL.

In the following paper I will endeavour to describe the system of indexing or digesting chemical literature and patents, now in use in the Classification Division of the United States Patent Office. This division was organised about a year ago to perfect the existing classification of United States patents. Under our laws, no valid patent can be granted for any new process, composition of matter, or chemical body, described in any printed publication prior to the inventor's discovery thereof, or more than two years prior to the date of his application for such patent; and, among other things, this division is now preparing an index or digest of literature and patents relating to chemical bodies and processes, for the use of the office in making its examinations of pending applications.

The system adopted is in the nature of a reference index rather than a classification, and is one elaborated by myself some five or more years since for another purpose, and on which we have been at work since last summer. I may add that our work was well advanced before my attention was called to the fact that there are great similarities between this system and that of Richter.

Generally speaking, in any comparison of digests or indexes that system may be considered best which, in the simplest, most certain, and most direct manner, puts the inquirer in possession of the desired information.

If chemical bodies each had but one instead of many names, and if, in chemical literature, one never met with bodies as yet unchristened, then undoubtedly, the dictionary plan, pure and simple, in which the names of bodies were alphabetically arranged and the references to literature and patents were collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use.

Practically, however, most bodies known to chemists have more than one name, many have several, and the names approved in prior decades are generally not the names in highest repute to-day; nor is it likely that the names now in use will in all, or even in most cases, remain those approved in future years.

Where a chemical compound has several names, were it possible to decide now (which perhaps might be done) which one of them was, on good scientific grounds, the most appropriate in view of present knowledge, and further (which, of course, could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but, while this might be done now in certain cases, who can guarantee that all the names approved to-day shall retain that approbation as our knowledge of chemical constitution is increased?

Evidently the dictionary plan, unmodified, is not the best, and some better system must be devised not open to these objections.

It would seem that the kind and number of the component atoms of a chemical compound are its most unvarying characteristics, and are subject only to the errors of chemical analysis; and that, therefore, these must form the most stable basis for any general scheme for the indexing or digesting of chemical literature; and this conclusion appears to have been independently reached by others than myself; as, for example, by

Richter in his recent and former work, and by Jacobsen and Stelzner, following Richter in the index numbers of *Berichte* for 1898 and 1899. We differ chiefly in the methods by which this principle receives practical application.

The simplest, most certain, and most direct system would be to re-cast the empirical formulæ of the compounds, writing the atoms in the alphabetical order of their chemical symbols, and to then arrange the formulæ on an alphabetical basis. For example, take the bodies $(\text{CH}_3)_2\text{C}_2\text{H}_2(\text{NO}_2)_2$, $(\text{CH}_3)_2\text{CHNO}_2$, $\text{KH}_3\text{C}_2\text{O}_4$, CH_3Cl , $\text{Cu}(\text{AsO}_2)_2$. Re-writing them as above, and arranging them alphabetically, we have As_2CuO_4 , CClH_3 , CCl_4 , $\text{C}_2\text{H}_3\text{KO}_4$, $\text{C}_3\text{H}_7\text{NO}_2$, $\text{C}_4\text{H}_8\text{N}_2\text{O}_4$.

It should be noted, however, that the compounds containing C and H, and broadly included in the domain of organic chemistry, constitute so large and important a class that we are fully justified in departing slightly from the alphabetical arrangement of chemical symbols, in order to thereby bring more closely together in the index bodies more or less closely related.

Generally speaking, an attempt to combine a dictionary or digest with a classification will be disastrous. We cannot sit on two stools at once, we will surely fall between them; and too much classification grafted on the dictionary or digest idea will give what is neither a good digest nor a good classification.

Classification, as applied to chemical compounds, should be supplementary to, and independent of, a mere digest or reference index.

In practice, therefore, I have modified the purely alphabetical scheme, and have adopted the following general rule for indexing:—

Reject the water of crystallisation, and re-write the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds write C first and H second; follow this re-written formula with the constitutional formula, when given, adding the water of crystallisation, if any, but arrange the titles alphabetically by the re-written formula.

The reason for disregarding water of crystallisation may be illustrated as follows:—The three bodies, Na_2SO_4 , or anhydrous sodium sulphate, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$, or Glauber's salt, and the heptahydrated salt, $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$, are in this way all indexed under the same indexing formula $\text{Na}_2\text{O}_4\text{S}$, and are thereby brought closely together, as they should be, in one place in the digest. If, on the other hand, water of crystallisation was taken into account for indexing purposes, the corresponding indexing formulæ would become $\text{Na}_2\text{O}_4\text{S}$, $\text{H}_{20}\text{Na}_2\text{O}_{14}\text{S}$, and $\text{H}_{14}\text{Na}_2\text{O}_{11}\text{S}$ respectively, and these three very closely related bodies would, in consequence, be widely separated in the digest, which result would, we think, be a very undesirable one.

Our index is being prepared on the card catalogue plan. The cards used are the regular Library Bureau standard card, No 33, size $7\frac{1}{2}$ by $12\frac{1}{2}$ c.m., or approximately 3 by 5 inches, without rulings except a single blue horizontal line, ruled $\frac{3}{8}$ of an inch below the top edge of the card.

The following is a sample set of cards as actually made out in a given instance, except in size.

ONE FORMULA CARD:

$\text{C}_{12}\text{O}_{18}\text{Fe}_2\text{O}_{12}$	or	$(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$
Ferric Acetate; Acetate of Iron;		
Klaproth's Iron Tincture; Tinctura		
Ferri Acetatis; Iron Tincture,		
Klaproth's.		

See "A Treatise on Chemistry." By H. E. Roscoe and C. Schorlemmer, vol. iii., "Organic Chemistry," Part I., page 505.

ONE POLYMER OR MULTIPLE FORMULA CARD:

$\text{C}_6\text{H}_9\text{FeO}_6$	Polymer	Class 2.
See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ or $(\text{C}_6\text{H}_9\text{FeO}_6)_2$		
Ferric Acetate.		

* Read before the Washington Section of the American Chemical Society, May 10, 1900. From the *Journal of the American Chemical Society*, xxii., No. 8.

TWO CLASSIFICATION CARDS:

Acetates

Ferric.

See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

Iron

Acetate of.

See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

FOUR SUBJECT-MATTER OR TITLE CARDS:

Ferric Acetate

See $C_{12}H_{18}Fe_2O_{12}$.

Klaproth's Iron Tincture

See $C_{12}H_{18}Fe_2O_{12}$.

Iron, Klaproth's Tincture of

See $C_{12}H_{18}Fe_2O_{12}$.

Tinctura Ferri Acetatis

See $C_{12}H_{18}Fe_2O_{12}$.

Considering first the formula card, it will be noted that in the formula the atoms are re-arranged in the alphabetical order of their chemical symbols, except that in carbon compounds C comes first, and H second; and that, had there been water of crystallisation in the formula, it would have been rejected. Then follows the constitutional formula, where the water of crystallisation, if any, would appear. Thus had the body been cupric acetate, the first line of the formula card would have been $C_4H_6CuO_4$ or $Cu(C_2H_3O_2)_2 \cdot H_2O$. Then follows under the blue ruling, all the names given for the body in question, and, finally, the reference, by volume and page, to the work indexed.

When a citation is to a patent instead of to a book or other printed work, the reference given will be about like this:—

See U.S. Patent No. 319082 to Fahlberg, dated June 2, 1885.

The arrangement of these cards in the card index is strictly an alphabetical one. Thus, all cards reading C_1 take precedence of C_2 , C_2 of C_3 , &c. In the series C_1 , &c., the order of arrangement would be:—

C_1AgNO ; C_1AgS ; $C_2Ag_2O_3$; C_1Br ; C_1ClH_2N ; C_1Cl_2O ; C_1Cl_4 ; C_1CuN ; C_2HAgO_2 ; C_1HBr ; C_1HCl_2I ; C_1HCl_3 ; C_2HAgNO_3S ; $C_2H_2Cl_2$; C_2H_2S ; $C_2H_3AsCl_2$; C_2H_3Br ; C_2H_3ClOP ; C_2H_3F ; C_2H_4 ; C_2H_4AsClO ; C_2H_4ClN ; $C_2H_4AlNO_8S_2$; C_2H_6ClN ; C_2H_6 ; $C_2H_3CaClO_2$; C_2H_4AgNO ; C_2H_6As ; $C_6H_4AgNO_2$; $C_6H_{12}O$; $C_{10}H_{15}Cl_2P$; $C_{22}H_{18}ClN_4O$; $C_{40}H_{32}N_4O_{12}S_2$; CdO_4S ; $ClCu$; ClH_2Hg_2NO ; DiN_3O_9 ; HKO_3S ; $KMnO_4$; PCl_3 ; PCl_5 ; &c.

The foregoing series will fully illustrate the method of arrangement.

The polymer or multiple formula cards perform the following function:—There are many bodies which analysis shows to be composed of certain elements in certain proportions, but for which theory at present indicates a formula containing two, three, or more times as many atoms. Thus, at one time the formula of ferric chloride was written $FeCl_3$, whereas it is now very often written Fe_2Cl_6 , and such doubled and tripled formulæ are very common.

In all cases where, in the formula as written, the exponents of all the atoms have a common divisor, after the doubled, tripled, or other form as found is used for preparing the formula card, the formula is then reduced to its lowest terms by dividing the exponents by their greatest common divisor, and a polymer or multiple formula card, made out in the form shown by the foregoing sample ("Class 2," "Class 3," &c., on the polymer cards, indicates the common divisor). In this way the index is rendered independent of any changes in the formula consequent upon future changes of view with reference to constitutional formulæ and other matters of theory.

A mere reference index or digest should in no way de-

pend upon any theory subject to future changes with advancing knowledge. Classification, on the other hand, must necessarily depend on theory, and must change as knowledge is increased.

These polymer cards are sorted in with the regular formula cards to form part of the formula division of the index or digest. We may illustrate the function of these cards thus:—Suppose ferric chloride had been found in the literature under the formula Fe_2Cl_6 , and so indexed, but no polymer card made out, and some one consulted the index under the formula $FeCl_3$; the reference, though in the digest, would not be found, but with the polymer card made out the inquirer by it would be referred to the card Fe_2Cl_6 , where the required references would appear. All the remaining cards compose the subject-matter or title index, comprised first of the classification cards, second of the regular subject-matter or title cards, and third of any general topics that it may be thought advisable to include in the alphabetical division of the index.

These cards require but little explanation, except that the general statement should be made that all references to the literature or patents of chemical bodies are intended to be entered on the formula card, and all the other cards are merely used as cross references, referring the inquirer to the formula card for all required information.

Classification, it will be noted, is attempted only to a limited extent now, but will be carried out much more completely hereafter, by a supplementary scheme not yet fully perfected—independent of, though based on, the reference index.

The present scheme, however, it will be observed, does incidentally bring together very many closely related carbon and other compounds, and arranges alphabetically, under such general titles as acids, alcohols, ethers, acetates, chlorides, &c., the specific bodies of the given class.

In practice, to use the digest, if the empirical formula of any compound is known, it must be re-written by the rule already given, and at once is disclosed the definite place in the formula index where the desired references, if digested, will be found entered upon the formula card.

If, on the other hand, one of the various names of the body is given, the subject-matter index is entered alphabetically, and a cross reference obtained to the re-written formula with which the formula index is entered for the required information.

The question arises, as between this system and such a one as that adopted in the *Berichte*, which one of them is the best; that is, the most practical for the intended uses? It may be said generally that the Patent Office needs the index for exactly the same purpose as the scientific or practical chemist; i.e., to obtain references to the literature concerning definite chemical bodies, where either the name or the chemical composition or both is given, so that the system best for the one use is probably also best for the other as well.

We consider our system to be preferable, certainly so at least for the Patent Office, and I may say that it was elaborated and adopted without any knowledge of the work of Richter as followed in the *Berichte* by Jacobsen and Stelzner.

In our system the arrangement of the formulæ is governed by the following general principles in the following order:—

- 1st. The number of C atoms } in carbon compounds.
- 2nd. The number of H atoms }
- 3rd. The alphabetical arrangements of the symbols of the remaining elements (including H in other than carbon compounds).

Practically, in indexing, or in using the digest as an index, the only thing to be remembered is, that in carbon compounds C comes first and H second, and that otherwise the re-arrangement of formulæ and the arrangement of such formulæ in the digest is always alphabetically by

the symbols, instead of by the names of the component elements.

That the *Berichte* system is much more complex will be seen at once. Other things being equal, we deem that system which is simplest to be the best, provided it achieves a result of equal value. The ideal system, we think, produces the best result with the minimum of labour, both mental and physical.

In re-writing the empirical formula by the *Berichte* or Richter system, one must remember the following arbitrary established order of precedence of certain of the chemical symbols; viz., C, H, O, N, Cl, Br, I, F, S, P, and this both in re-writing the formulæ and in entering the table. One must also consider the number of carbon atoms in the compound, the number of different varieties of atoms, and various other things as well.

Thus, for example, in the Richter system, the following are the principles which govern, in the order of their relative importance:—

- 1st. The number of C atoms.
- 2nd. The number of different kinds of atoms other than C.
- 3rd. The arbitrary arrangement of ten of the component elements in the following order; viz., C, H, O, N, Cl, Br, I, F, S, P, all taking precedence over the remaining elements.
- 4th. The arrangement of all other component elements in the alphabetical order of their chemical symbols.
- 5th. The arrangement of chlorides, bromides, amides, anilides of carbon acids, acetyl and benzoyl derivatives, oximes, phenylhydrazones, &c., under the formulæ of their corresponding bases.
- 6th. The arrangement in general, of salts, either under the formulæ of their bases, or of their acids.
- 7th. The arrangement of salts of quaternary ammonia bases under the formulæ of their corresponding hydroxides.

(To be continued).

CATALYSIS IN CONCENTRATED SOLUTIONS.*

By J. M. CRAFTS.

THE study of the catalytic action of acids in very dilute solutions has led to the discovery of a number of simple relations between ionic dissociation, chemical affinity, and electrical conductivity, and the conclusion is universally accepted that the active agent is the hydrogen ion. The ratio of the velocity of the reaction to the concentration of the catalyst is nearly constant in dilute solutions of strong acids, but when ionic dissociation is diminished by increasing concentration, or in the case of weak acids by the presence of bodies which reduce the concentration of hydrogen ions, the ratio of velocity to concentration diminishes; a small acceleration has, however, been observed when certain salts are added to the solutions of strong acids. Most of the subjects for experiments, such as the decomposition of esters, the inversion of sugar, &c., do not admit of the employment of very concentrated acid solutions, because the catalyst would then enter into the reaction, forming by-products.

It seemed interesting to study the hydrolysis of the sulphonic acids by means of chlorhydric acid and other strong acids, because here the reaction is catalytic in the sense that it is induced by the presence of a strong acid which does not enter into the final products, nor does it even form intermediate products in the same evident way as in esterification by sulphuric acid or in the oxidation of sulphurous acid through the medium of nitrous fumes, nor does the degree of concentration of the catalysing agent change the nature of the products, which are only sulphuric acid and hydrocarbon.

The results given below show that the rapidity of the reaction instead of being proportional to the concentration of the catalyst, rises to a thirty-fivefold greater rapidity when 38 per cent chlorhydric acid solution is employed instead of 19 per cent, and a very remarkable result was obtained by adding to a 38 per cent chlorhydric acid solution one-half its weight of zinc chloride, the rapidity of the reaction being then raised more than threefold.

It is thus apparent that increased concentration and other influences which must be supposed to diminish ionic dissociation, promote to a high degree the rapidity of the hydrolytic action, and this fact would point to the inference that the hydrolysis is promoted by $\text{HCl} + \text{H}_2\text{O}$, and not by the hydrogen ions, unless some other predominant and preparatory reaction can be attributed to dehydrating agents like chlorhydric acid, sulphuric acid, and zinc chloride. The study of this hypothesis has been undertaken, but seems to demand an extended series of experiments before an opinion can be formed, and it is desired to give in this preliminary notice a description of experiments which establish a sharp distinction between catalysis in dilute and concentrated solutions. It is possible that the newly observed phenomena may be quite different from catalysis, and may require another name, but the old one has been made to hide so many mysteries that it will serve to cover this one also, until a new theory of the reaction can be founded upon a larger number of experiments.

I will give the results of some 150 measurements in sealed tubes chiefly at 100° , and will leave aside a larger number of experiments which were made by passing steam through sulphuric acid solutions of sulphonic acids at different temperatures.

The work will be interrupted for a few months, and it is desired to reserve the field until the projects, which will be indicated for further experiments along the same line, can be executed and the data obtained for explanation, or at least for correct formulation of this interesting reaction.

Experimental Results.

On heating in sealed tubes at 100° , the metaxylene-sulphonic acid (1 : 3 : 4) gives an easily measurable rate of decomposition with chlorhydric acid of concentrations varying between 43 per cent and 13 per cent HCl gas; and the intervals of time which it is necessary to heat in order to decompose 10 per cent of the sulphonic acid, vary between thirty minutes and more than 100 hours, according to the strength of the acid. Benzene and toluene-sulphonic acids do not react at this temperature, paraxylene-sulphonic acid acts very slowly, and the sulphonic acids of the higher homologues of benzene act too rapidly at 100° , and, moreover, these acids are only partly soluble in strong chlorhydric acid even at 100° . For these reasons the first series of determinations was made with the metaxylenesulphonic acid, $\text{C}_8\text{H}_9\text{SO}_3\text{H} + 2\text{H}_2\text{O}$. The crystals of the acid can be kept for any length of time exposed to the air with only slight hygroscopic changes of weight.

A mode of preparation, which was found much more advantageous than the passage by the barium salt, consists in using directly the solution obtained by heating, during two hours at 100° , 2 parts of common sulphuric acid and 1 part hydrocarbon. The immediate product is added cautiously, to prevent heating, to common chlorhydric acid (containing about 38 per cent HCl) cooled to zero or below. Paratoluenesulphonic acid, the common forms of metaxylene and pseudocumene sulphonic acids, and the sulphonic acids of paraxylene and mesitylene, are nearly insoluble in strong cold chlorhydric acid, and the fine crystalline precipitate can easily be washed with pure cold chlorhydric acid with little loss until entirely free from sulphuric acid. Exposure for two days on a glass plate suffices to remove all traces of chlorhydric acid, and to leave the pure sulphonic acids crystallised with their normal proportions of water of crystallisation. The crystalline powder so obtained can be dissolved in water

* *Journal of the American Chemical Society*, xxiii., No. 4.

and re crystallised without change of weight. Paratoluenesulphonic acid has 1 molecule of water of crystallisation; the other acids named have 2 molecules. Paratoluenesulphonic acid so prepared melts at 102° ; metaxylenesulphonic acid (1:3:4) at 59.8° ; paraxylenesulphonic acid melts at 86° ; pseudocumenesulphonic acid (1:3:4:5) at 112° .

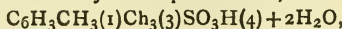
The Hydrolysis, $C_8H_{10}SO_3 + H_2O = H_2SO_4 + C_8H_{10}$.—In each experiment a weighed quantity of the sulphonic acid was sealed with a weighed quantity of chlorhydric acid, or some other substance or acid as a catalyst, in a glass tube of about 1 c.m. diameter, which had been calibrated with weighed amounts of the hydrocarbons, xylene, cumene, &c.

The determinations were made, after heating a definite period, by measuring the height of the layer of hydrocarbon set free. Certain precautions were taken relative to the solubility of the hydrocarbon in the acid solution both hot and cold, and the time required for the complete separation of the dissolved hydrocarbon on cooling. A few control determinations of the sulphuric acid set free were also made, but in this preliminary notice it is not necessary to enter into the details of these operations, because even considerable errors of measurement and impurity of the sulphonic acids would not disguise the nature of the reaction, which it is designed to show.

A well determined and constant temperature was obtained by using the ebullition of pure substances, water, and benzene, under atmospheric pressure. The tubes were always heated in contact with the liquid bath, and allowance was made for the time (about three minutes) required for a thermometer enclosed in a similar tube to take the temperature of 79° or 99° . If the test is made by plunging the glass tube, containing a thermometer and filled with liquid, in a metal tube heated by boiling water to a constant temperature but only containing air, the transfer of heat through the air layer to the glass tube is so slow that nearly an hour is required for the thermometer to reach 100° .

A. Experiments with Metaxylenesulphonic Acid and Chlorhydric Acid.—In the following experiments (Nos. I.—XIII.), the temperature was 99.7 — 100° . The hours from the commencement of heating, and the corresponding percentages of decomposition are given. The latter was usually determined by measuring the hydrocarbon set free in a tube which had been calibrated at the same place with known weights of the same hydrocarbon. It was usually necessary to wait some hours for the complete separation of the hydrocarbon which had dissolved at a high temperature in the acid liquid, but appeared to be almost completely separated in the cold, so that the readings became constant after intervals of an hour.

I. 10 grms. metaxylenesulphonic acid,—



+ 75 grms. chlorhydric acid (10 per cent. HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	0.0	136	8.7
32	2.2	156	8.7
64	4.3	172	9.4
104	5.6	212	10.0
120	6.5		

The apparent retardation of the decomposition during the first sixteen hours is probably only due to the solubility in the acid mixture of the first fraction of xylene, about 0.04 gm. If this is the case, about 1 per cent should be added to all the measures. The decomposition with a measurable rate of speed up to about 10 per cent, and from that point a decomposition of only 0.6 per cent in forty hours, seems to indicate the presence of an impurity, possibly $C_6H_3CH_3(1)SO_3H(2)CH_3(3)$, which decomposes more rapidly, while the pure acid, $C_6H_3CH_3(1)CH_3(3)SO_3H(4)$, which remains is not decomposed by 10 per cent chlorhydric acid solution.

II. Ten grms. metaxylenesulphonic acid + 75 grms. chlorhydric acid (13.1 per cent HCl). 0.43 gm. xylene was added before heating in order to saturate the acid liquid; the height of the layer of xylene was noted after shaking, and was subtracted from subsequent readings.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
16	1.9	136	10.2
32	2.4	152	12.0
48	4.2	172	13.8
64	5.4	188	15.7
88	7.9	204	17.4
104	9.0	222	18.7
120	10.2		

The series was terminated by the breaking of the tube.

III. Ten grms. metaxylenesulphonic acid + 70 grms. chlorhydric acid (19 per cent HCl). No corrections were made for the solubility of xylene in the acid solution in this and in the subsequent experiments.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.0	144	40.5
20	6.4	160	44.6
24	9.0	176	47.8
40	14.7	192	51.1
56	20.0	208	54.8
72	21.7	224	58.1
88	25.7	240	61.0
104	30.7	256	63.8
128	36.4	272	66.3

IV. Ten grms. metaxylenesulphonic acid + 30 grms. chlorhydric acid (10.3 per cent HCl) + 8.75 grms. sulphuric acid.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	1.0	96	31.8
8	2.5	112	36.2
12	4.0	133	40.8
16	7.0	155	46.3
32	12.6	175	51.9
48	17.6	191	55.4
64	23.1	231	63.9
80	27.7	279	70.4
		327	77.0

V. Ten grms. metaxylenesulphonic acid + 93 grms. chlorhydric acid (19 per cent HCl) + 37.5 grms. zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.0	24	30.9
8	13.4	28	31.1
12	16.0	32	34.8
16	22.0	36	38.8
20	26.0	40	42.3

VI. Twenty grms. metaxylenesulphonic acid + 90 grms. chlorhydric acid (25 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	3.6	52	55.2
8	10.0	56	58.0
12	16.0	60	60.9
16	20.3	64	64.8
20	27.1	68	67.7
24	32.0	72	69.8
28	35.6	88	77.7
32	39.2	104	84.1
36	44.9	120	86.9
40	46.3	136	90.1
44	48.1	152	91.5
48	52.0		

VII. Ten grms. metaxylenesulphonic acid + 515 grms. chlorhydric acid (25 per cent HCl).

Hours.	Xylene. Per cent.
4	2
16	22
20	29

A large bulb with a narrow neck of very thick glass was used. The calibration of the somewhat conical neck was less exact, and the readings were more uncertain than in a tube.

VIII. Twenty grms. of metaxylenesulphonic acid + 70 grms. chlorhydric acid (31.4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	14.2	28	83.1
8	29.7	44	92.0
12	47.6	60	96.1
16	57.9	76	95.6
20	68.3	92	95.9
24	76.9		

IX. Ten grms. metaxylenesulphonic acid + 550 grms. chlorhydric acid (31.4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	6.3	10	35.2
2	9.4	14	44.8
6	20.9	18	60.0

X. Twenty grms. metaxylenesulphonic acid + 70 grms. chlorhydric acid (38.4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	34.9	48	91.8
8	67.7	64	93.0
12	83.7	80	94.5
16	88.7		

XI. Ten grms. metaxylenesulphonic acid + 38 grms. chlorhydric acid (38.4 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
$\frac{1}{2}$	0	$\frac{5}{2}$	48.9
$\frac{1}{4}$	3	$\frac{6}{2}$	56.5
$\frac{3}{4}$	5.7	$\frac{7}{2}$	60.8
1	8.4	$\frac{8}{2}$	66.6
$1\frac{1}{2}$	14.0	$\frac{9}{2}$	70.6
2	18.6	$10\frac{1}{2}$	72.1
$2\frac{1}{2}$	23.5	$11\frac{1}{2}$	74.7
3	28.5	$13\frac{1}{2}$	79.7
4	37.2	$15\frac{1}{2}$	81.0
$4\frac{1}{2}$	41.0	$17\frac{1}{2}$	82.0

XII. Ten grms. metaxylenesulphonic acid + 39 grms. chlorhydric acid (43 per cent HCl).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
2	38.2	9	90.7
4	68.6	10	91.0
5	77.2	14	92.8
6	86.0	18	94.2
7	89.5	22	97.3
8	90.4	38	97.7

XIII. Ten grms. metaxylenesulphonic acid + 38 grms. chlorhydric acid (38.4 per cent HCl) + 19 grms. ZnCl_2 .

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
1	28.1	6	92.2
2	55.0	10	96.4
3	75.9	14	97.5
4	86.1	18	99.8
5	90.3	34	99.4

XIV. Temperature 80.2°. Ten grms. metaxylene-sulphonic acid + 36 grms. chlorhydric acid (38.4 per cent HCl) + 18 grms. zinc chloride.

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	6.0	20	49.6
8	15.6	24	57.5
12	27.9	28	65.3
16	38.2	32	72.2

(To be continued).

HISTORY OF VOLUMETRIC ANALYSIS.

PROF. L. L. DE KONINCK, of Liège, has published in the *Bulletin de l'Association Belge des Chimistes* (vol. xv., Jan.-Février, 1901), a sketch of the origin and growth of volumetric analysis which shows impartial study and bibliographic accuracy.

In the labours of Wenzel and of Richter on the reciprocal relations of bases and acids in producing neutral salts (1777 to 1792), is found the law of definite proportions, which lies at the basis of analysis by volume, yet even the germs of this method are lacking. The earliest publication of a volumetric process was by Descroizilles, in 1795, with the title, "Description et Usage du Bertholli-mètre," and appeared in the "Journal des Arts et Manufactures," vol. i. (reprinted in pamphlet form, Paris, 1802). The instrument herein described, named after the French chemist Berthollet, was devised to measure the value of chlorine water and of bleaching solutions by means of a solution of indigo of known strength. To Descroizilles then belongs the credit of first replacing weights of reagents by volumes of their solutions, as well as of devising graduated cylinders for measuring the liquids. He also had constructed instruments called *acétimètres* and *milli-litrimètres*, differing in their graduation; as an indicator in valuing the acid of vinegar he employed litmus-paper. And he was the first to apply this principle of volumetric determination to commercial analyses, yet he did not adopt the fundamental principle which consists in obtaining the weight of a substance by determining the amount of a corresponding reagent, and which allows the direct preparation, by weighing the reagent, of a liquid of definite value. This general principle was first used by Lampadius; the latter describes in his "Handbuch zur Chemischen Analyse der Mineralkörper" (Freyberg, 1801), the method of determining the amount of soda in a sample of crude, natural soda from Hungary; he added sulphuric acid, drop by drop, to a solution of the substance, until it was neutralised, as shown by curcuma, and he then calculated from the weight of the acid used that he had 98 grains of pure soda. This was published five years before Descroizilles made known his first note on alkalimetry in the *Annales de Chimie*, 1806, vol. lx.

This new method, which Dr. de Koninck calls "*titrage stathmométrique*," was not appreciated at its true value by Pfaff, Berzelius, and contemporary chemists, and it was not until Gay-Lussac's researches that its importance in analytical operations was established. Gay-Lussac, without perceiving the universality of the method, saw the possibility of applying it to several special cases, and became the veritable founder of volumetric processes. In 1824 he used this system in valuation of bleaching-powder, in 1828 in analysing commercial potashes, and in 1832 he made the important application to determining silver. He improved on the empiric methods of Descroizilles, and by the invention of the *burette*, graduated after the metric system, gave the process a truly scientific basis.

The next persons to perfect and extend the method were H. Schwarz, of Breslau (who had worked in the laboratory of Pelouze, one of the pupils of Gay-Lussac), who published in 1850 a treatise devoted to "Titrimethode," and Friedrich Mohr, whose classic work, dated 1855, has since

passed through seven editions, and has been translated into several languages.

Dr. de Koninck in his admirable essay treats of many other details, and so far as possible establishes priority in several instances. He shows that fourteen years after Thomas Clark, of Aberdeen, had patented his soap-test for the hardness of water, Boutron and Boudet submitted a paper to the French Academy of Sciences on "Hydrotimétrie," and on the recommendation of such eminent men as Dumas, Boussingault, Chevreul, and others, Messrs. Boutron and Boudet received a prize of 2000 francs for their contribution, notwithstanding it was little more than an adaptation of the process of Clark!

De Koninck's paper concludes with a bibliography of 116 titles. H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 13, September 23, 1901.

Distribution of Acidity in the Stem, Leaf, and Flower of a Plant.—A. Astruc.—There exist in most vegetables free or combined acids, which are soluble in distilled water and easily estimated by titration with an alkaline solution, in presence of phenolphthalein. The author's researches on the distribution of these acids show (1) that the acidity of leaves, more so than that of stems, is in inverse proportion to their age, the youngest consequently being the most acid; (2) that in the same leaf the maximum acidity is found at and round the growing point; (3) that the acidity of the stem diminishes in proportion to the distance from the summit; (4) that the acidity of the flower decreases as the flower changes from a bud into the fully expanded blossom. From the author's experiments it seems always to be the youngest parts of a plant which are the most acid.

No. 14, September 30, 1901.

Formation of Acids in Vegetables.—M. Berthelot and G. André.—The authors' researches show that, in reality, vegetable liquids tend generally to be acid, but the amount of this acidity in no degree represents the total acid present. By far the greater proportion of acid is present in the state of combination with bases, forming soluble salts with potassium, and either soluble or insoluble salts—according to the acid—with lime. In order to obtain the total acidity of a plant, it is not only necessary to titrate the juices against a standard alkali, but also to estimate the alkali present in the ashes of the plant. The mineral acids are usually present in mere traces. The total acidity can thus be obtained by summation.

Calculation of the Heat of Volatilisation and Heat of Fusion of certain Elements.—M. de Forcrand.—

From the general relation $\frac{L+S}{T} = \frac{(l+s)M}{T} = 30$, which

gives the molecular weight M , when l , s , and T are known, the value of $L+S$ can be calculated if values for T and M are known. This calculation is interesting in certain cases, notably in the case of phosphorus. No determination of L has been made for this element, which prevents a rigorous comparison between the corresponding thermometric constants of phosphorus and nitrogen, for example. The heat of fusion, S , of phosphorus is accurately known, and the molecular weight, M , is admitted to be 124 for P_4 at boiling-point (560° absolute). Applying

the above formula, $\frac{(l+s)124}{560} = 30$ is obtained; from which $l = 130.4$ cal. and $L = 16,176$ cal. The same method of

calculation may be applied to arsenic, selenium, and carbon; but, in the case of carbon, the calculation becomes very uncertain, on account of the vagueness of the boiling-point.

Formation of an Isatinic Derivative of Albumin.—Julius Gneзда.—In a former paper, the author announced the formation of indolic bodies by means of albumin treated with acids. As albumin, when treated with hypochlorous acid, evolves nitrogen, and as a portion of the nitrogen always remains in combination, it is presumed that, when treating albumin with hypochlorous acid, an indolic body remains. Hypochlorous acid being a feeble acid, it may be assumed that the results of its action on albumin may be applied to various conclusions with regard to the constitution of albumin. The author supposes that the new body formed in this way is a chlorisatine, on account of its following reactions:—With potash, it gives a magnificent reddish violet coloration; and when added to silver nitrate and ammonia, it gives again a red powder. These reactions are characteristic of chlorisatine.

MEETINGS FOR THE WEEK.

THURSDAY, 31st.—Chemical, 8.30. Frankland Memorial Lecture.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Potassium Metabisulphite.—A correspondent wishes to have the chemical formula and mode of preparing this salt.

SOUTH AUSTRALIAN SCHOOL OF MINES AND INDUSTRIES.

Applications are invited up to October 29th for the position of INSTRUCTOR OF CHEMISTRY, METALLURGY, and ASSAYING. Salary, £400. Particulars on application to State Agent of South Australia, 1, Crosby Square, London, E.C.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the next EXAMINATIONS of the INSTITUTE OF CHEMISTRY, for persons desirous of qualifying themselves to be Public and Technical Analysts, will be held at 30, Bloomsbury Square, London, W.C., in January, 1902.

The Examinations are open only to such candidates as have complied with the regulations.

The Intermediate Examination will occupy at least four days, commencing on Tuesday, January 7th.

Examinations in the following branches of the Final Examination for the Associateship (A.I.C.) will extend over at least four days, and may commence on either January 7th or 14th:—

(a) Mineral Chemistry; (b) Metallurgical Chemistry; (c) Physical Chemistry; (d) Organic Chemistry; and (e) the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy.

(The Final Examination in the branch of Biological Chemistry is held in October of each year).

Applications for admission to the January Examinations should be forwarded to the Registrar not later than Tuesday, December 3rd, 1901, on which day the list of candidates will be closed.

(By Order of the Council)

30, Bloomsbury Square, London, W.C.
October, 1901.
RICHARD B. PILCHER,
Registrar and Secretary.

* * "The Regulations for the Admission of Students, Associates, and Fellows of the Institute of Chemistry" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C., price One Shilling.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2188.

VOLUMETRIC ESTIMATION OF MANGANESE.

By HUGH RAMAGE, B.A., A.R.C.Sc.I.

A PAPER on the above subject, by Jos. Reddrop and the present author, was published in the *Journ. Chem. Soc.* for 1895, p. 268. A nitric acid solution of the sample is prepared, the acid being about 4N, and oxidised in the cold by "sodium bismuthate." After filtration the permanganic acid is reduced by "a slight excess" of hydrogen peroxide, and the excess of this reagent determined by titration with N/10 potassium permanganate. Sulphuric acid may be present during oxidation, &c., and also hydrofluoric acid (Ibbotson and Brearley, *CHEM. NEWS*, vol., lxxxii., p. 269). The solution must be free from chlorine. The procedure was described for the analysis of ferromanganese, spiegels, wrought-iron, steel, and pig-iron, and also for "ores, &c., of manganese." The method has been successfully applied to the analysis of manganese bronzes.

The experiments by which this method of analysis was perfected were made in the Crewe works laboratory in 1891, and the method has been in constant use since that time. Further experiments were made by the author in the summer vacation of 1894, and after this work the paper was written.

No question of inaccuracy has been raised regarding the results obtained in the analysis of ferromanganese and spiegels, but the results have been questioned in the analysis of steel and iron. It has been found, for instance, that the gravimetric method gave higher results than this method. The original paper, however, explained the cause of this. The work of Hartley and the author* on the spectrographic analysis of iron, iron ores, &c., has proved the fact that traces of nickel, cobalt, copper, lead, metals of the alkaline earths, and alkalis, are frequently present in iron ores, and that part of these metals pass into the iron smelted from them. These metals are wholly or partially precipitated with manganic hydrate in the gravimetric process, for this has been proved by spectrographic analysis. Samples of steel, made from ores containing traces of these metals, were found to contain 0.024 per cent of copper and 0.049 per cent of nickel and cobalt. These quantities would raise the results appreciably.

Ibbotson and Brearley have called attention to the fact that the authors of the original paper (*CHEM. NEWS*, vol. lxxxii., p. 269), "offer no reason why, for steels and low manganiferous alloys, the hydrogen peroxide is added to the permanganate, and for spiegels and highly manganiferous alloys the permanganate is filtered into the peroxide. The distinction is a necessary one; can it be explained?" The fact that higher results are obtained by the latter procedure has caused doubts to be raised regarding the accuracy of the results obtained by the original method. Experiments have been made to discover the cause of the above differences, and to further test the accuracy of the results obtained by the original method. My friends in the Crewe laboratory have shown great interest in this investigation, and have made many experiments. More recently the author has been free to assist, and, with Mr. Ryder's most able assistance, has completed the work. All the possible sources of error we could think of have been considered.

These experiments have established the fact that the original method gives accurate results. The best results are obtained by adding an excess of from 1.5 to 3.0 c.c. of the hydrogen peroxide solution; the difference from the true result does not then exceed 0.01 per cent. Each c.c. of hydrogen peroxide outside these limits causes an error of about 0.01 per cent.

The method which will be found most suitable for steel and iron works is as follows:—

Wrought-iron, Steel, and Pig-iron.

Dissolution of Sample.—Weigh out 1.1 grm. of the sample, and place it in a beaker or boiling-tube; add 30 c.c. of dilute nitric acid (approx. 5N), and boil. If a part remains undissolved, decant the solution, filter off carbonaceous matter if necessary, and add more nitric acid up to 25 c.c. If the sample dissolves completely use the 25 c.c. of acid to wash the tube. The free acid in the solution thus prepared is about 4N. If the sample contains much silicon care must be taken, when boiling, not to unduly concentrate the acid, or the silicic acid will separate in a form which blocks up the filter.

Oxidation and Titration.—Cool the solution in a beaker to about 16°, oxidise with 2 grms. of "sodium bismuthate," stir for three minutes, and filter through an asbestos filter into a clean flask. Add hydrogen peroxide solution (approx. N/10 in N nitric acid), from a burette until the reddish colour disappears; then add from 1.5 to 3.0 c.c. in excess, and titrate with N/10 potassium permanganate. The hydrogen peroxide must be standardised by the process described in the original paper.

Each c.c. of hydrogen peroxide (N/10) reduced by the sample = 0.1 per cent of manganese.

The reddish colour mentioned above is produced by a secondary reaction during the titration, probably between the permanganic acid and the reduced manganous nitrate. A small quantity of manganic salt appears to be formed, and the yellow colour of this masks the colour of the permanganic acid. This yellow solution is more difficult to reduce than the solution of permanganic acid, and the tinctorial power of the compound is much less than that of the acid; hence the necessity for adding an excess of hydrogen peroxide. Experiment shows that ferrous sulphate produces a much larger proportion of this yellow compound than hydrogen peroxide does.

With reference to the point raised by Ibbotson and Brearley it may be stated that the authors of the original paper conducted several analyses in both ways, and obtained results in close agreement with one another. The method of titration was recommended because the quantity of manganese in the samples we received varied between the widest limits, and we could not be sure of adding "a slight excess" of hydrogen peroxide to the flask before filtration. It has been discovered in the recent experiments that hydrogen peroxide and ferric nitrate react in some unknown way, and that for each c.c. of the former added to a solution containing 1.1 grm. of steel or iron in nitric acid, about 0.1 c.c. is immediately reduced. This reaction exerts a slight influence on the results obtained by the original method in the analysis of iron and steel, and the instructions to "add a slight excess of hydrogen peroxide" are now given more precisely.

Another small error has been discovered in the original method which tends to correct the foregoing. This error is due to a slight reduction of permanganic acid which takes place during, and after, filtration. In amount it is between 0.01 and 0.015 per cent, and the excess of hydrogen peroxide recommended corrects this. The cause of this reduction is not quite clear, but it may be prevented by more complete oxidation of the solution of the sample. This was effected as follows:—After the sample had dissolved in 30 c.c. of dilute nitric acid, the solution was cooled to about 40°. Half a grm. of sodium bismuthate was then added and the solution heated to boiling, and boiled for three minutes. It was then cooled to the ordinary temperature, and a slight excess of sulphurous

* *Proc. Roy. Soc.*, vol. lx., p. 393; *Journ. Iron and Steel Inst.*, 11., 1897; *Engineering*, September, 1897, p. 395; *Trans. Roy. Soc.*, vol. cxvii., p. 502.

acid added to reduce the precipitated oxide of manganese. After oxidation with 1.5 grm. of "sodium bismuthate," and filtration in the usual way, hydrogen peroxide was added from a burette until the reddish colour disappeared and left a clear yellow coloured solution. An excess of from 0.6 to 1.0 of hydrogen peroxide was then added, and the solution titrated with N/10 potassium permanganate. The end of the reaction was more sharply defined in these experiments than in the ordinary method. It was, with some samples, necessary to add more than 0.5 grm. of sodium bismuthate.

The following test experiments were made by this method. The "Farnley iron" contained 0.013 per cent of manganese, and the test solutions were prepared by adding N/10 potassium permanganate to this iron before adding the nitric acid to dissolve it:—

N/10 potassium permanganate added to 1 grm. of Farnley iron.	Hydrogen peroxide solution.	Potassium permanganate required. N/10.	Manganese, per cent.		
			Present.	Found.	Difference.
C.c.	C.c.	C.c.			
2.5	3.0	0.35	0.263	0.259	-0.004
5.0	6.0	0.75	0.513	0.513	0
10.0	10.5	0.15	1.013	1.019	+0.006
15.0	16.0	0.5	1.513	1.518	+0.005

The following are the results obtained by this more refined method, and for comparison those obtained by the original method in ordinary laboratory practice:—

Sample.	Combined carbon. Per cent.	Manganese, per cent.	
		Most accurate method.	Original method.
File steel, No. 17 ..	0.90	0.433	0.44
Sample, No. 66 ..	0.58	0.762	0.76
Sample, No. 163 ..	0.42	1.388	1.41

No further tests of this nature were considered necessary. The method followed in the Crewe laboratory was to add the hydrogen peroxide from a pipette, in 5 c.c. at a time, until the colour was discharged. The excess, therefore, never exceeded 5 c.c.

The accuracy of the method appears now to be beyond question, and as the whole analysis has been completed in twelve minutes by the ordinary method it may be recommended for use in all steel and iron works. Recent work has given prominence to the part played by manganese in soft steels, and a method for the estimation of this metal, which is both accurate and rapid, should prove of great value to the manufacturers and to engineers.

St. John's College, Cambridge.

Congress of Russian Naturalists and Doctors of Medicine.—On January 2nd, 1902 (December 20th, 1901, Old Style), the Eleventh Congress of Russian Naturalists and Doctors of Medicine will be opened at St. Petersburg. The Executive Committee consists of the President, Prof. N. A. Menchoutkine; the Vice-President, Prof. A. A. Inostranzeff; and the Secretaries, Profs. I. I. Borgman and W. T. Chewiakoff. The Congress will be divided into the following Sections:—Mathematics and Mechanics, Astronomy and Geodesy, Physics, Physical Geography, Chemistry, Geology and Mineralogy, Botany, Zoology, Anatomy and Physiology, Geography, with a sub-section on Statistics, Agronomy, Scientific and Hygienic Medicine. The Congress will sit from the 2nd to the 12th January, 1902. General meetings will be held on the 2nd, 8th, and 12th January, and the Sections will meet on the 3rd, 4th, 5th, 6th, 9th, 10th, and 11th of January. All those who wish to take part in the meetings as members of the Congress are invited to send their full addresses, and their subscriptions (three roubles), together with the name of the Section they wish to join, to the Executive Committee of the Congress, at the University of St. Petersburg, before December 15th, 1901.

ON A SYSTEM OF INDEXING CHEMICAL LITERATURE;

ADOPTED BY THE CLASSIFICATION DIVISION OF THE U.S. PATENT OFFICE.*

By EDWIN A. HILL.

(Concluded from p. 205).

By way of comparison, I have taken from the pages of the *Berichte* index a number of bodies, with the formulæ written and arranged as there shown, and have re-written and re-arranged them on our own classification division plan.

Formulæ taken from the Berichte Index.

(Pages refer to *Berichte*, No. 19, of 1899).

C ₁	CO ₂	p. 3448.	C ₃	C ₃ H ₂ O ₂ N ₅	p. 3459.
	CCl ₄			C ₃ H ₂ OBr	
	CS ₂			C ₃ H ₂ OCl	
	CHN			C ₃ H ₂ OBr	
	CHCl ₃			C ₃ H ₂ O ₄ S	
	CHBr ₃			C ₃ H ₂ N ₂ S	
	CH ₂ O			C ₃ H ₂ ON	
	CH ₂ N ₄			C ₃ H ₂ NS	
	CH ₂ I ₂			C ₃ H ₂ ON ₂	
	CH ₃ N ₅			C ₃ H ₂ O ₂ N ₃ S	
C ₂	CH ₃ Br	p. 3449.	C ₄	C ₄ H ₂ ONBr	p. 3460.
	CH ₄ O ₃			C ₄ H ₂ O	
	CH ₅ N			C ₄ H ₁₂ N ₂	
	COCl ₂			C ₄ N ₂ H ₄	
	CNBr			C ₄ H ₂ O ₄ N ₂	
	CHO ₂ Cl			C ₄ H ₁₃ ON	
	CHNS			C ₄ H ₂ ON ₃ S	
	CO ₄ N ₂ Br ₂			C ₅ H ₁₂	
	CHO ₄ N ₂ Br			C ₅ H ₄ O ₂	
	C ₂ H ₂			C ₅ H ₁₁ N	
C ₃	C ₂ Cl ₆	p. 3452.	C ₅	C ₅ H ₁₄ N ₂	p. 3470.
	C ₂ HN ₃			C ₅ HN ₄ Cl ₃	
	C ₂ Cl ₆ Hg ₆			C ₅ H ₂ O ₃ Cl ₄	
	C ₂ I ₂ Hg ₂			C ₅ H ₁₅ O ₂ N	
	C ₂ HOC ₃			C ₅ H ₂ ON ₄ Cl ₂	
	C ₂ H ₂ O ₈ N ₄			C ₆ H ₆	
	C ₂ H ₂ N ₃ Cl			C ₆ H ₁₄	
	C ₂ H ₃ O ₂ Cl ₃			C ₆ Cl ₆	
	C ₂ H ₃ O ₂ Br			C ₆ H ₂ O ₆	
	C ₂ H ₄ O ₇ S ₂			C ₆ H ₆ O ₂	
C ₄	C ₂ H ₄ N ₂ Cl ₂	p. 3454.	C ₆	C ₆ H ₆ N ₄	p. 3475.
	C ₂ H ₅ O ₂ N			C ₆ H ₆ Cl ₆	
	C ₂ H ₅ N ₂ Cl ₃			C ₆ H ₆ S	
	C ₂ H ₆ O ₃ S			C ₆ H ₁₅ P	
	C ₂ H ₆ NBr			C ₆ H ₃ OCl ₃	
	C ₂ HO ₂ Cl ₃ Hg ₃			C ₆ H ₃ NC ₄	
	C ₃ H ₆			C ₆ H ₂₀ O ₂ As ₂	
	C ₃ H ₂ O			C ₆ H ₂ ONBr ₃	
				C ₆ H ₁₄ O ₂ NBr	
				C ₆ H ₅ OCl ₂ SP	

In the foregoing arrangement, the formulæ are given in the same order as in the *Berichte*, other formulæ which come in between these being omitted; and in the following table these formulæ are re-written and re-arranged on the plan which we have adopted, a few formulæ not found in the *Berichte* index being added to illustrate the application of our scheme to inorganic bodies.

Formulæ Re-written and Arranged on the Plan adopted by the Classification Division, U.S. Patent Office.

The re-written formula is, in our digest, generally followed by the empirical or constitutional formula as usually written by chemists, but from lack of space I have omitted the constitutional formula in many cases in the following table:—

* Read before the Washington Section of the American Chemical Society, May 10, 1900. From the *Journal of the American Chemical Society*, xxii., No. 8.

C ₀ Not in Berichte index.	H ₀	AgCl
		AgMnO ₄
C ₁	H ₀	AlH ₄ NO ₈ S ₂ or NH ₄ Al(SO ₄) ₂ +12H ₂ O
		AsH ₂ KO ₄ or KH ₂ AsO ₄
C ₂	H ₀	AuCl ₄ K or KA _u Cl ₄
		BNaO ₂ or NaBO ₂
C ₃	H ₀	BaN ₂ O ₆ or Ba(NO ₃) ₂
		Br ₂ OSe or SeOBr ₂
C ₄	H ₀	Br ₂ Zn or ZnBr ₂
		CBrN or BrCN
C ₅	H ₀	CBr ₂ N ₂ O ₄ or C(NO ₂) ₂ Br ₂
		CCl ₂ O or COCl ₂
C ₆	H ₀	CCl ₄
		CHBrN ₂ O ₄ or CHBr(NO ₂) ₂
C ₇	H ₀	CHBr ₃
		CHClO ₂ or COCl.OH
C ₈	H ₀	CHCl ₃
		CHN or HCN
C ₉	H ₀	CHNS or CN.SH
		CH ₂ I ₂
C ₁₀	H ₀	CH ₂ N ₄
		CH ₂ O or COH ₂
C ₁₁	H ₀	CH ₃ Br
		CH ₃ N ₅
C ₁₂	H ₀	CH ₄ O ₃
		CH ₅ N or NH ₂ (CH ₃)
C ₁₃	H ₀	CO ₂
		CS ₂
C ₁₄	H ₀	C ₂ Cl ₆
		C ₂ Cl ₆ Hg ₆ or C ₂ Hg ₆ Cl ₆
C ₁₅	H ₀	C ₂ HCl ₃ Hg ₃ O ₂ or CHg ₃ Cl ₃ CO ₂ H
		C ₂ HCl ₃ O or CCl ₃ .CHO
C ₁₆	H ₀	C ₂ HN ₃
		C ₂ H ₂
C ₁₇	H ₀	C ₂ H ₂ ClN ₃
		C ₂ H ₂ N ₄ O ₈ or C ₂ H ₂ (NO ₂) ₄
C ₁₈	H ₀	C ₂ H ₃ BrO ₂
		C ₂ H ₃ Cl ₃ O ₂ or CCl ₃ .CH(OH) ₂
C ₁₉	H ₀	C ₂ H ₄ Cl ₂ N ₂ or (CH ₂ Cl) ₂ N ₂
		C ₂ H ₄ O ₇ S ₂ or CHO.CH(SO ₃ H) ₂
C ₂₀	H ₀	C ₂ H ₅ Cl ₃ N ₂
		C ₂ H ₅ NO ₂ or C ₂ H ₅ NO ₂
C ₂₁	H ₀	C ₂ H ₆ BrN or N(CH ₃) ₂ Br
		C ₂ H ₆ O ₃ S or C ₂ H ₅ (SO ₃ H)
C ₂₂	H ₀	C ₂ H ₂ l ₂
		C ₃ HN ₅ O ₂ or $\begin{array}{c} \text{N}=\text{C}-\text{N}-\text{N} \\ \quad \quad \quad \\ \text{HN}-\text{C}-\text{CO}-\text{O} \end{array}$
C ₂₃	H ₀	C ₃ H ₂ O or CHO.C ₂ H
		C ₃ H ₃ BrO
C ₂₄	H ₀	C ₃ H ₃ BrO
		C ₃ H ₃ ClO
C ₂₅	H ₀	C ₃ H ₃ N ₃ O ₂ S
		C ₃ H ₆ or CH ₃ .CH.CH ₂
C ₂₆	H ₀	C ₃ H ₆ BrNO or N.CO.C ₂ H ₅ .HBr
		C ₃ H ₆ N ₂ S
C ₂₇	H ₀	C ₃ H ₉ NO or OH.CH ₂ .CH ₂ .NH.CH ₃
		CH ₃ -CH-SH
C ₂₈	H ₀	C ₃ H ₉ NS or $\begin{array}{c} \text{CH}_2-\text{NH}_2 \\ \\ \text{CH}_3-\text{CH}-\text{SH} \end{array}$
		C ₃ H ₁₂ N ₂ O or OH(CH ₃) ₃ N.NH ₂
C ₂₉	H ₀	C ₄ H ₂ N ₂ O ₄
		C ₄ H ₄ O or $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \\ \quad \\ \text{CH}-\text{CH} \end{array}$
C ₃₀	H ₀	C ₄ H ₇ N ₃ OS
		C ₄ H ₁₂ N ₂ or (CH ₃) ₂ N.N(CH ₃) ₂
C ₃₁	H ₀	C ₄ H ₁₃ NO or N(CH ₃) ₄ OH
		C ₄ H ₄ N ₂
C ₃₂	H ₀	C ₅ HCl ₃ N ₄
		C ₅ H ₂ Cl ₂ N ₄ O
C ₃₃	H ₀	C ₅ H ₂ Cl ₄ O ₃
		C ₅ H ₄ O ₂
C ₃₄	H ₀	C ₅ H ₁₁ N

C ₅	H ₁₂	C ₅ H ₁₂ or CH ₃ (CH ₂) ₃ CH ₃
		C ₅ H ₁₄ N ₂
C ₆	H ₁₅	C ₅ H ₁₅ NO ₂ or N(CH ₃) ₃ (C ₂ H ₄ .OH)OH
		C ₆ Cl ₆
C ₇	H ₂	C ₆ H ₂ Br ₃ NO
		C ₆ H ₂ O ₆
C ₈	H ₃	C ₆ H ₃ Cl ₃ O or C ₆ H ₂ Cl ₃ (OH)
		C ₆ H ₃ Cl ₄ N or C ₆ H ₄ .Cl ₄ NH ₂
C ₉	H ₅	C ₆ H ₅ Cl ₂ OPS or SP(OC ₆ H ₅)Cl ₂
		C ₆ H ₆
C ₁₀	H ₆	C ₆ H ₆ Cl ₆
		$\begin{array}{c} \text{N}-\text{CH} \\ \quad \\ \text{HC} \quad \text{C}-\text{N}-\text{CH}_3 \\ \quad \quad \equiv \text{CH} \\ \text{N}-\text{C}-\text{N} \end{array}$
C ₁₁	H ₁₄	C ₆ H ₆ O ₂ or C ₆ H ₄ (OH) ₂
		C ₆ H ₆ S or C ₆ H ₅ .SH
C ₁₂	H ₁₅	C ₆ H ₁₄ or (CH ₃) ₂ CH.CH(CH ₃) ₂
		C ₆ H ₁₄ Br
C ₁₃	H ₂₀	C ₆ H ₁₅ P or P(C ₂ H ₅) ₃
		C ₆ H ₂₀ As ₂ O ₂ or (CH ₃) ₃ (OH)As ₂ OH(CH ₃) ₃
C ₁₄	Cl	ClO ₃
		Cl ₂ Ni or NiCl ₂
C ₁₅	Co	CoS
		C ₁ O ₄ Pb or PbCrO ₄
C ₁₆	Cr	Cr ₂ K ₂ O ₁₆ S ₄ or Cr ₂ (SO ₄) ₃ K ₂ SO ₄ +24H ₂ O
		CuN ₂ O ₆ or Cu(NO ₃) ₂
C ₁₇	H	FeK ₂ O ₈ S ₂ or FeK(SO ₄) ₂
		HK ₂ or K ₂ H
C ₁₈	H ₂	H ₂ MoO ₄
		H ₂ N or NH ₃
C ₁₉	H ₃	HgNO ₃
		IKO ₃ or KIO ₃
C ₂₀	H ₄	K ₂ NiO ₈ S ₂ or NiSO ₄ +K ₂ SO ₄ +6H ₂ O
		MoO ₄ Pb or PbMoO ₄
C ₂₁	H ₅	Na ₂ O ₃ Si or Na ₂ S ₂ O ₃
		OPb or PbO
C ₂₂	O	O ₂ Pd or PdO ₂
		O ₃ Te or TeO ₃
C ₂₃	Si	SSi or SiS

As a practical test of the two systems take the six following bodies, re-write them first by our system and find them in our table; then re-write them by the *Berichte* rules and find them in the *Berichte* table; and the demonstration of the superior simplicity of our system will be complete. The bodies are:—

1.		SP(OC ₆ H ₅)Cl ₂
2.		C ₆ H ₂ Cl ₃ (OH)
3.		CHg ₃ Cl ₃ CO ₂ H
4.		CN.SH
5.		N.CO.C ₂ H ₅ .HBr
6.		$\begin{array}{c} \text{N}=\text{C}-\text{N}-\text{N} \\ \quad \quad \quad \\ \text{HN}-\text{C}-\text{CO}-\text{O} \end{array}$

This comparison speaks louder than words, and I think most chemists will agree with me that our system affords to the inquirer with the minimum of technical knowledge the maximum of information, in the surest manner, and with the minimum of mental and physical labour, and without the danger that a future change in theory will mislead the future user of it. In other words, the use of the digest is as far as possible independent of all theory, and founded only on unchanging facts.

Let me here call attention to the point that, in the *Berichte* system, the formulæ of very many large classes of bodies—such as salts, amides, anilides of acids, &c.,—have no representation in the index. Their formulæ do not appear in it at all; but only their names, which are classified under the different formulæ of some related body; so that in a given case, unless one remembers all these various classes of excepted bodies, if forgetting any of these things he re-writes the formula, and enters the

Berichte digest or index with it, thus re-written, he finds none of the matter indexed. He must first remember that the body sought is not indexed under its own, but under some different formula of a body more or less closely related to it; that is, that the body belongs in some one of these many excepted classes, and then, after determining under what base or acid it will be found, he must enter the table with the re-written formula, not of the body itself, but of the given base acid or other body to which it is now supposed to be related, although advancing knowledge may hereafter prove this view as to supposed relationship to be erroneous.

Moreover, in the case of a body of which the number and kind of the component atoms are known, but as to the constitution of which little or nothing is known, while the body may be correctly entered in the *Berichte* index under the formula of some base or acid or other supposedly related body, it would evidently never be found, because not knowing its constitution, we do not know the base or acid under which it is indexed, and so would not find it in the table.

In our system, every chemical body indexed is represented in the digest or table by its re-written empirical formula. No bodies are indexed as sub heads under the formulæ of other compounds. The indexing, and conversely, the finding of the body in the index, is rendered absolutely independent of any theories of constitution whatever, and made to depend solely on the kind and number of the component atoms, arranged alphabetically by their symbols, except that in carbon compounds, C comes first and H second. Nothing can be more simple.

No serious attempt is made, however, to make the system, which is merely intended to be a reference index, at once a classification and also an index as well; that is, classification is not pushed beyond the point where it begins to encroach on the digest idea; and any such attempt, I believe, will surely fail to fully fulfil either function in the highest degree. In a good index, the classification idea must be kept subordinate. Hence, it follows that from our point of view, the *Berichte* system, as a mere digest or index, as well as that of Richter and all other similar systems, is inferior to ours in the points indicated; while as systems of classification, they can not but be inferior to such as are founded on proper lines. Such systems can be worked out without being hampered by the digest or dictionary idea, and which important work—classification proper as distinguished from a mere digest or index—we hope to be able to take up at some future time, on a comprehensive scale, as supplementary to the present work in hand.

It would be manifestly unfair, however, in this comparison of systems, to overlook the fact that both in the field covered, and in the intended use, the two systems are not exactly the same. Richter's system is designed for, and applied solely to, the bodies of organic chemistry for the use of specialists in that branch familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference—C, H, O, N, Cl, Br, I, F, S, P—is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulæ, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done—that is, establish no order of preference whatever, with the one exception, of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

Moreover, Richter's system is more adapted to the needs of those who are studying bodies as a class, and to whom classification is of greater importance; while our system is specially adapted to the needs and requirements

of those who are merely searching for references to the literature of specific chemical bodies—particularly those bodies the empirical formulæ of which are known, but as to the constitution of which little, if any, information is at hand.

The approval of our system, therefore, does not necessarily imply that it is a criticism of or shall supersede that of Richter. Because of these differences in the field covered and in the intended use, the two systems have really no serious quarrel; and where ours is applied to organic bodies, the Richter formula could also be given on the cards prepared on our system to facilitate reference to the *Berichte*, and the Richter Lexicon, with its 75,000 titles of organic compounds.

In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I cannot see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts of the Chemical Society*, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by re-written formulæ as one of the component parts of a general scheme for chemical indexing, would be that to re-write or re-arrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulæ with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier additions of his "Lexicon," and adopted and approved in the *Berichte* Indexes, and other publications, as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an enlarged edition of his earlier work. So that, with such backing as Richter and the *Berichte*, it would seem as if the objection was not as valid as might at first appear.

Moreover, in our system it is an unvarying rule that the re-arranged formula is never used or written, whether on cards or elsewhere, without being immediately followed by the empirical or constitutional formulæ, so far as the same are known or inferred; so that an objection which might have force, were nothing but the re-written formulæ given in the digest or on the index cards, loses its force when the ordinary formula, so familiar to the chemist, is

always an invariable accompaniment of the new and unfamiliar indexing formulæ.

As soon as the idea is fully grasped that the re-written formula is merely an arbitrary arrangement, in the nature of a position indicator, determining position in a mere reference index to literature and nothing more, the chemical sense will be no longer offended. The justification for its use lies in the fact that such a formula unerringly indicates one, and one only, definite and specific place in the index where we are to look for all references, with a certainty that no other character, name, or title of the body can afford. With other systems we are somewhat uncertain where to look for our information; with this system all uncertainty at once disappears.

Personally I should be glad to see a general scheme of indexing current chemical literature carried out at some future time for the benefit of American chemists, under the auspices, for instance, of the Smithsonian Institution, along these general lines which have been blocked out in our Classification Division, modified or improved perhaps by the combined wisdom and experience of the American Chemical Society.

For example, the Smithsonian Institution might publish an annual index to current chemical literature, divided into a formula division, arranged along some such lines as here suggested, and a subject-matter or title division, in which all names and subjects were alphabetically arranged, and the names of chemical bodies all cross-referenced into the formula index, all references to the literature of chemical bodies being collated under the unvarying formula of the body, and not under one of its various and varying names.

Such an index should cover the leading chemical periodicals—such works as *Berichte* and the *Abstracts of the Chemical Society*, and the more important chemical publications of the year.

The vast army of chemical workers in our universities, laboratories, and corporate and government offices and institutions, state and national, should be enlisted in the work, each willing worker assigned some special publication or portion of same, and be supplied with standard library bureau cards and general instructions; and the cards as prepared sent in to the central bureau established here in Washington, where, after being sorted into place in the receiving cabinets, and with proper editing, they would form the basis from which would be compiled the annual index volume.

These volumes would probably be less of a digest and more of an index than the present *Abstracts of the Chemical Society* or the *Berichte*, and would cover a somewhat different field than either.

Lastly, these annual volumes should be sold at cost price, so as to become a working tool in the hands of all the chemical workers in the country.

I may here briefly refer to a special development of this work now being carried out in our Patent Office Index. We have procured two copies each of the *Berichte* Indexes for 1898 and 1899. The separate titles in the formula portion of these indexes are in most cases small enough to be cut out and pasted on our standard indexing cards, and still leave room enough at the top to re-write the formula on our own plan. We are also considering the application of this system of cutting and pasting from two duplicate copies to the new Richter "Lexicon" with its 75,000 titles, and possibly to the four volumes of the last edition of Watts's "Dictionary," Thorpe's "Dictionary of Applied Chemistry," the yearly abstract volumes of the *Journal of the London Chemical Society*, and such other works of general reference as it may be found advisable.

But to return, in conclusion, to the idea of a central bureau at Washington, supervising the indexing of chemical literature, would not some such plan, properly matured, and carried out to a successful completion, be a work worthy of the great scientific institution of the national capitol, founded expressly for the dissemination

of useful knowledge, and be directly in line with their publication in past years of the indexes to the literature of specific chemical bodies, which has so much redounded to their credit? It seems to me at least that it would be a work worthy of their best endeavour, and of whose great utility there could be no question whatever.

CATALYSIS IN CONCENTRATED SOLUTIONS.*

By J. M. CRAFTS.

(Concluded from p. 207).

B. Experiments with Metaxylenesulphonic Acid Heated with Sulphuric Acid at 100°.—

XV. Ten grms. metaxylenesulphonic acid + 35 grms. dilute sulphuric acid (25 per cent H_2SO_4) were heated twenty hours at 100°. There was no sign of separation of xylene.

XVI. Ten grms. metaxylenesulphonic acid + 112 grms. dilute sulphuric acid (50 per cent H_2SO_4).

Hours.	Xylene. Per cent.	Hours.	Xylene. Per cent.
4	4.2	56	69.6
8	13.9	60	71.4
12	21.2	64	74.4
16	27.8	68	76.3
20	34.5	72	78.1
24	40.6	76	79.3
28	44.2	80	81.7
32	47.8	96	85.4
36	52.7	112	86.0
40	56.3	128	87.2
44	59.3	144	88.4
48	64.2	160	88.4
52	66.6	176	88.4

XVII. Ten grms. metaxylenesulphonic acid + dilute sulphuric acid (75 per cent H_2SO_4).

Soon after heating, the well known phenomenon took place between the diluted sulphuric acid and the sulphonic acid; a lighter layer of a viscous liquid rose to the top, and this was covered by a smaller layer of xylene. The viscous layer which separated contained 5.5 per cent of dissolved xylene, and the remainder had nearly the composition $H_2SO_4 + 2H_2O$ (33 per cent) + $C_8H_{10}SO_3 + 2H_2O$ (67 per cent). It is more probable, however, that most of the water should be regarded as combined with sulphuric acid, and the greater part of the metaxylenesulphonic acid must be anhydrous, on account of its power of dissolving xylene. This view is confirmed by the fact that the crystalline hydrated sulphonic acid dissolves on gently warming in sulphuric acid diluted with enough water to make 75 per cent H_2SO_4 , and then an acid separates later on heating, giving the upper viscous layer.

These experiments suggest the idea that all dehydrating agents may bring the crystalline hydrated sulphonic acids into an anhydrous state, and that the anhydrous form may exist in solution, and perhaps be more susceptible of hydrolysis than the hydrated acids. This hypothesis will be investigated.

C. Metaxylenesulphonic Acid Heated to 100° with Nitric Acid.—

XVIII. Ten grms. metaxylenesulphonic acid + common nitric acid, diluted with an equal weight of water, were heated three hours at 100° in a sealed tube. There was no sign of xylene, and only traces of insoluble nitro-derivatives. The pressure of gas due to oxidation was not very strong.

Thus, nitric acid has no action favouring hydrolysis to be compared to that of a molecular equivalent of chlorhydric or sulphuric acid.

PERCENTAGE DECOMPOSITION OF METAXYLENESULPHONIC ACID HEATED TO 100° WITH CHLORHYDRIC ACID.

The Relation between Concentration of the Acid Solutions and the Rapidity of the Hydrolysis.

Curves were plotted of all these series of experiments, and the accompanying table gives the time required in each case to decompose 5, 10, 15, &c., per cent of the sulphonic acids.

In Experiments II. to XVI., the first vertical column of the table gives the percentages by weight of HCl gas in the chlorhydric acid solution; the second column gives the weights of acid solution to which in each case 10 grms. of crystallised sulphonic acid were added; and the third vertical column gives for Experiment IV. a weight of H₂SO₄ added to the solution, while for Experiments V., XIII., and XVI. weights of ZnCl₂ were added.

The next eighteen vertical columns give the hours and decimal fractions of an hour required to decompose 5, 10, 15, &c., per cent of the sulphonic acid.

The last column gives the velocity constants, calculated, not from the figures of the table, but from the means of the constants given by each experimental measure, rejecting those of less than 10 and more than 80 per cent decomposition, because at the two extremities the results are less accurate.

A very remarkable relation appears between the velocity constants and the concentration of the chlorhydric acid which promotes the action (as a catalyst?).

For the percentages of HCl between 13 and 31 the velocity increases fourfold for each successive increment of 6 per cent HCl. The rate appears to be less rapid for higher percentages, but the upper limit of the law may perhaps be extended by more careful measures. Unpublished experiments confirm this relation for other sulphonic acids and extend it to lower percentages of HCl.

Mathematically stated, the relation is expressed by the formula: the logarithm of the velocity constant is a linear function of the percentage concentration of chlorhydric acid.

Since the sulphonic acids have nearly as strong a chemical affinity as chlorhydric acid, it was thought that they might catalyse themselves, and the decomposition might be related to the concentration. Only two experiments have been made, but they serve to confirm this idea:—

1. Five grms. metaxylenesulphonic acid were dissolved in 2½ grms. of water, and were heated at 100° for forty hours. The sulphuric acid set free was 1.9 per cent of the amount corresponding to complete decomposition. No xylene was visible in the tube, but it separated out on diluting with water.

2. Five grms. of metaxylenesulphonic acid were dissolved in 100 grms. water and heated to 100° for forty hours. The sulphuric acid set free was only 0.1 per cent. Thus, concentration in these experiments gives rise to a rapidly increasing rate of decomposition.

With metaxylenesulphonic acid a change of position of the SO₃H group, if such change can be brought about catalytically, would complicate the reaction, since the susceptibility to decomposition is greatly increased when the SO₃H group is placed between the two side chains.

The series of experiments will be extended to other temperatures, and the more tedious—but likewise more accurate—method of weighing the sulphuric acid set free instead of measuring the amount of hydrocarbon will be used.

If we attempt to estimate the differences and the similarities in the modes of catalytic action of strong acids in concentrated or in weak solutions, it will be convenient to do so under the headings of Ostwald's definition of catalysis.

1. *Reactions which are Accelerated or Retarded by Catalysis take place also without a Catalyst.*—Experiments are evidently impossible with substances which take years for the transformation of 1 per cent, and conclusions can usually only be drawn from the form of reaction curves of measurable velocities, but it appears probable that the regularity of the decomposition of sulphonic acids without by-products will make it possible to obtain

	Percentage of chlorhydric acid.	Weight of liquid. Grms.	Added. Grms.	Per cent.																Velocity constant. Unit of time, 100 hours.			
				5.	10.	15.	20.	25.	30.	35.	40.	45.	50.	55.	60.	65.	70.	75.	80.		85.	90.	
II.	13.0	75	—	55.0	118.0	182.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.089	
III.	19.0	70	—	17.0	29.0	44.0	61.0	80.0	100.0	120.0	140.5	162.0	187.0	210.0	234.0	264.0	—	—	—	—	—	0.39	
IV.	10.0	30	8.75 H ₂ SO ₄	13.0	25.0	40.0	55.0	70.5	92.0	113.0	132.0	151.5	170.0	189.0	207.0	233.0	—	—	—	—	—	0.40	
V.	19.0	93	37.5 ZnCl ₂	4.5	6.5	10.0	14.0	18.5	24.0	30.0	37.5	—	—	—	—	—	—	—	—	—	—	1.43	
VI.	25.0	45	—	5.0	8.0	11.0	14.5	18.5	23.0	28.0	33.5	39.0	45.5	52.0	58.5	65.5	73.5	84.0	92.0	—	—	1.59	
VII.	31.4	35	—	—	—	4.2	5.3	6.4	7.6	9.0	10.3	11.6	13.0	14.6	16.4	18.5	20.8	23.3	25.8	29.1	35.0	5.75	
VIII.	31.4	35	—	—	—	4.2	5.3	6.4	7.6	9.0	10.3	11.6	13.0	14.6	16.4	18.5	20.8	23.3	25.8	29.1	35.0	5.75	
IX.	31.4	550	—	0.8	2.2	3.6	5.0	6.6	8.3	10.0	11.9	13.9	15.4	16.8	18.0	—	—	—	—	—	—	5.10	
X.	38.4	35	—	—	—	—	—	—	—	—	4.0	4.5	5.0	5.5	6.1	6.8	7.5	8.5	9.5	10.8	—	14.1	
XI.	38.4	38	—	0.5	1.2	1.6	2.1	2.6	3.1	3.8	4.3	5.0	5.6	6.4	7.1	8.1	9.4	11.2	14.3	—	—	12.9	
XII.	43.0	39	—	—	—	—	—	—	1.8	1.95	2.1	2.3	2.6	2.8	3.2	3.7	4.0	4.7	5.2	—	—	31.0	
XIII.	38.4	38	19 ZnCl ₂	—	—	—	0.8	0.9	1.0	1.2	1.4	1.5	1.7	2.0	2.2	2.4	2.6	2.9	3.4	—	—	47.8	
When Heated to 80° with Chlorhydric Acid (38.4 per Cent) and 50 per Cent ZnCl ₂ .																							
XIV.	38.4	36	18 ZnCl ₂	4.0	6.0	7.6	9.4	11.0	12.8	14.6	16.4	18.3	20.5	22.6	25.0	27.4	30.6	33.6	—	—	—	—	3.2
When Heated to 100° with Sulphuric Acid (50 per Cent).																							
XVI.	50.0	35	—	4.0	6.0	8.25	11.0	14.0	17.0	20.5	24.0	29.0	33.5	38.5	44.0	50.0	57.5	65.5	76.5	94.0	—	—	2.1

When Heated to 80.1° with Chlorhydric Acid (38.4 per Cent) and 50 per Cent ZnCl₂.

When Heated to 100° with Sulphuric Acid (50 per Cent).

3.2

47.8

useful observations near the border line, where the action is almost imperceptible.

2. *Reactions in Opposite Directions leading to an Equilibrium must be Equally Influenced by Catalysis.*—The hydrolysis of sulphonic acids in presence of sulphuric acid and water would belong under this rule if the reaction were reversible; but this is probably not the case, since the synthesis is direct, while the decomposition is indirect by influence of H_2SO_4 (catalysis?). The data for 50 per cent sulphuric acid given in the preceding table show that the limit of the action is very near complete decomposition (88 per cent), while experiments made by heating xylene with sulphuric acid of 50 per cent concentration to 100° proved that the reverse action does not take place perceptibly.

Even the action of a 75 per cent sulphuric acid solution on xylene is an exceedingly slow one, and stops when only a few per cent of the xylene are transformed into the sulphonic acid. The hydrolysis of sulphonic acids by means of chlorhydric acid tends to complete decomposition, nor can any evidence be obtained of an inverse reaction.

3. *The Catalytic Influence is nearly Proportional to the Concentration of the Catalyst.*—The chief object of this paper is to show that this rule does not apply to the case of concentrated acids, and that here the facts are directly opposed to the assumption that hydrolysis is caused by hydrogen ions. In the experiments cited, the relation between concentration of acid and effect rises like the tension of a gas partially combined with water, and the effect of high concentration in aqueous solution of chlorhydric acid alone, and especially with addition of zinc chloride, recalls the activity imparted to gases condensed on platinum or palladium. Ostwald discusses the action of these metals under the same heading as catalysis attributed to the ions of hydrogen, iron, manganese, &c., and OH ions, and also places ferments and enzymes beside them, saying there is no great doubt that the laws governing the action of these bodies are not essentially different from those of inorganic catalysts.

Taking these definitions together, they apply in very few points to the case of hydrolysis by concentrated acids.

The question of ionic dissociation presents new aspects in this case. Usually the compounds subjected to catalysis have been, like sugar and esters, incapable of any marked degree of dissociation in aqueous solution. The sulphonic acids, on the contrary, are dissociated to nearly the same degree as the strongest acids, when in dilute solution, and although very little is known of the dissociation of strong acids in concentrated solution, it well may be considerable. If hydrolysis only takes place upon undissociated molecules, then the increased rapidity due to high concentration of the acid solution and to addition of zinc chloride may be ascribed to the prevention of the dissociation of the catalysed body, while that of the catalyst subsists to a certain degree.

Experiments at different temperatures and with more sensitive bodies, like mesitylenesulphonic acid, which acts at low temperatures and with weaker acids, may throw some light upon this subject.

The usefulness is evident of a minute study of the difference of behaviour of the sulphonic acids, for it may obviously lead to methods of separation of the hydrocarbons and the acids. Several authors have described such methods for the separation of meta- and paraxylene, and I have found during this series of experiments that mesitylenesulphonic acid, when heated to 80° for fifteen minutes with 38 per cent chlorhydric acid, is almost wholly decomposed, while pseudocumenesulphonic acid, heated under the same circumstances, gives no sign of the separation of pseudocumene after five hours. Armstrong has used this difference of action to separate the two hydrocarbons by heating their sulphonic acids with chlorhydric acid at 100° , but the statement attributed to him in "Beilstein" (II., 29) is incorrect, namely, that pseudocumenesulphonic acid is not decomposed by

heating for one hour with strong chlorhydric acid at 100° . There is difficulty in getting the rate for the first hour, because the pseudocumenesulphonic acid does not dissolve rapidly in strong chlorhydric acid at 100° , but the following determinations show the rate for subsequent hours:—

Ten grms. pseudocumenesulphonic acid, heated to 100° , with 35 grms. chlorhydric acid (38.4 per cent HCl), gave the following results:—

Pseudocumene.		Pseudocumene.	
Hours.	Per cent.	Hours.	Per cent.
1½	24.7	6½	95.9
2½	42.3	7½	101.6
3½	61.8	8½	103.8
4½	76.6	9½	100.3
5½	90.5	10½	100.3

The impossible results, 103.8 per cent, &c., may be due to the fact that a small amount of anhydrous sulphonic acid separates out and dissolves in the layer of hydrocarbon, and is only slowly decomposed. All the results are too high for the same reason, and a similar error, but a very small one, attaches to the preceding experiments with xylene. The fact that pseudocumenesulphonic acid loses a little water on long standing may also account for the above result.

Armstrong's observations were undoubtedly exact, but he is misquoted by Beilstein. He really states (*Ber. d. Deut. Chem. Ges.*, xi., 1697) that an oily layer is formed by adding water to the immediate product of the action of sulphuric acid upon pseudocumene, and this oil, added to an equal volume of common chlorhydric acid, is not decomposed by heating one hour to 100° . No strength of acid is given, but the oily layer so described contains anhydrous pseudocumenesulphonic acid in solution in aqueous sulphuric acid, and the water present probably suffices to dilute the acids to the point where no perceptible decomposition takes place during one hour at 100° .

The name catalysis has been used after much hesitation, and it is only meant to imply that the rapidity of the action does not seem to be determined by the ordinary chemical forces of the bodies undergoing change, but rather that these forces are set in action in a peculiar way by an outside agent.

THE USE OF ALUMINIUM AS AN ELECTRICAL CONDUCTOR.

THE high price which copper has attained during the past few years, owing to a combination of natural and artificial causes, has drawn attention to the use of aluminium as an alternative conductor for the transmission of electric energy.

In order to make a proper comparison between copper and aluminium, from the point of view of their cost, we must take into consideration their densities and their different conductivities. If we take the average for the two metals in France, we arrive at the conclusion that, for equal conductivities, an aluminium line will cost 1000 francs, while a similar line of copper would only cost 798 francs. Aluminium is therefore dearer than copper in this country.

In America, however, considerable quantities of aluminium have been sold within the last few years at a very low price, which brings the ratio between copper and

aluminium to $\frac{1325}{1000}$ for an equal conductive capacity; this fact explains the facility with which the electricians of the New World have been able to adopt the white metal as a conductor. It must be remarked, however, that at the present time, and until the price has fallen considerably lower with regard to copper, there can be no question of using aluminium for a covered insulated conductor; still it is already in great demand for aerial lines.

The following are the details of some of the pure aluminium cables already installed on the other side of the Atlantic :—

At the Falls of Niagara there are two aluminium conductors. These two lines are short, and are known to give very satisfactory working results.

The Hartford Electric Light and Power Company has an aluminium line from its central station at Tariffville to Hartford, a distance of 17.7 kilometres. The diameter of the cable used is 0.0187 metre, and it weighs about 422.5 kilograms. per kilometre.

The aluminium conductor belonging to the Snoqualmie Falls Power Company has been frequently described in the technical press. It runs from the Falls to the two towns of Tacoma and Seattle. Its total length is 54.716 kilometres. The aluminium used was alloyed with 1.5 per cent of copper, and the increased tenacity obtained by this alloy permitted the safe use of cables of 36.5 m.m. to 45.6 m.m.

The Blue Lakes Power Company has an aluminium conductor in use between its central station at Blue Lakes and Sockton, a distance of 57.934 kilometres. The original line has been replaced by a new one of greater conductivity; 446 tons of metal were used for the new line. At 1 fr. 45 centimes per pound, this represents a total of 1,510,000 frs. (or 41,925 frs. per mile) for the metal alone.

One of the most interesting systems for the transmission of power in the United States, in which aluminium is used, is that of the Telluride Power Company.

This company produces its current at Provo in Utah, and distributes it through a circuit of 128.75 kilometres to the mines at Mercur and Tintic.

The following are the names of a few other American companies in which aluminium is used, or is on the point of being substituted for copper :—

1. The North Yuba Power Company, 101.385 kilometres;
2. The Municipal Supply Company, 28.967 kilometres;
3. The Big Cotton Wood Power Company;
4. The Standard Electric Company.

This latter company has been invited to instal a plant to supply San Francisco with electricity from a generating station to be situated in the mountains of Sierra Nevada, at a distance of over 240 kilometres away.

The success of this project depends on the possibility of maintaining the tension of 60,000 volts.

It has been decided to use aluminium cables for the purpose, and the plans have all been prepared.

In the greater number of these installations the difficulty of soldering the aluminium has been overcome by the use of mechanical joints. The MacIntyre sleeve joint has been generally adopted.

An examination of the principal installations where aluminium is used as a conductor shows the very great progress that has been made.

If this metal is sufficiently durable, and if its price continues to diminish, it will doubtless become an important rival to copper in this new field of usefulness.—*Revue Générale des Sciences*, Year XII., No. 19, October 15th, 1901.

THE ESTIMATION OF PLATINUM AND IRIIDIUM IN PLATINUM ORES.

By MM. LEIDIÉ and QUENNESSEN.

THE method devised by M. E. Leidié for the extraction and separation one from the other of the metals of the platinum group is of a general character, but it is principally intended for the solution of the most difficult cases in which the material is more or less completely insoluble in the solvents usually employed (*Comptes Rendus*, vol. cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9).

A much more simple case occurs in practice; that is to say, on the small scale the estimation of platinum in its ores, and on the large scale the commercial extraction of platinum. M. Leidié's method can be simplified, therefore, in the following manner :—

To obtain the metals in the form of chlorides we attack the ore with hot aqua regia (nitric acid D=1.32 1 part, and hydrochloric acid D=1.18 3 parts), until nothing more can be dissolved; the solutions are then evaporated, first on a sand-bath until they are of a syrupy consistence, then in a Wiessnegg oven at 105–110° until quite dry; the residue is taken up with water and filtered.

The method described by M. Leidié is then applied. We will briefly describe this method. The solution, heated to about 70°, is treated with nitrite of sodium until neutral to litmus, then with carbonate of sodium until no further precipitate is formed; it is then boiled, and filtered to separate all the metals which do not belong to the platinum group. A current of chlorine is then passed through the solution, which has been made alkaline with soda; then heat to 70–80°; this drives off the osmium and ruthenium in the form of volatile peroxides. The solution is neutralised with hydrochloric acid, and a further quantity of nitrite of sodium is added to re-form the metals which may have been partially transformed into chlorides, into nitrites.*

Estimation of the Platinum.—Instead of now saturating the solution with chloride of ammonium, as in the original process, we add chloride of potassium (about 30 to 35 per cent); the rhodium and iridium are precipitated in the state of double nitrites of potassium, which are insoluble in solutions of alkaline chlorides, like the corresponding nitrites of ammonium. The solution is then filtered, and the nitrites of platinum and palladium are transformed into chlorides by means of hydrochloric acid, taking the precautions that have already been pointed out. The saline mass is taken up with boiling water. The solution, containing platinum and palladium in the state of double chlorides, is then made alkaline with a little soda, and boiled in the presence of a slight excess of formol, so as to precipitate the two metals in the black or metallic form; the precipitate is collected on a filter, calcined, reduced with hydrogen, and then taken up with aqua regia. The solution is evaporated down and taken up with water, then treated with NH_4Cl to precipitate the platinum. This metal is then estimated by any of the ordinary known methods.

This modification of M. E. Leidié's original method was devised for the purpose of doing away with the driving off of the chloride of ammonium by heat, an operation which is attended by a good deal of trouble when operating on the large scale, and which may easily be accompanied by a loss of the metal if it is not very carefully carried out. Further, the reduction by formol cannot be effected in the presence of NH_4Cl , as the evolution of ammonia, caused by the action of the soda, transforms the salts of palladium and platinum into palladoamines and platinoamines. Now, as these ammoniated bases cannot be reduced either by formol, or even by the dissolved alkaline formates, it is necessary, for separating the whole of the metals, to evaporate the whole to dryness with a formate—and that several times over—as done by Ste.-Claire Deville and Debray; thus we should only come across another set of difficulties.

* It can be seen that all the foreign metals are completely precipitated, and that the metals of the platinum group are completely transformed into double nitrites, by the fact that the filtrate no longer gives a precipitate in the cold with sulphydric acid. It may happen in a case when large quantities of nitrite have been used, that a little copper will remain in solution; this metal would then be in the form of a cuprous salt not precipitable under these conditions. We then add a little peroxide of hydrogen to the solution and heat to boiling-point; the cupric oxide formed is then entirely precipitated. In the operations which follow it is necessary to avoid too great concentration of the solutions, as some platinum might then be lost. The solution is of a convenient degree of concentration when it only just commences to crystallise at the edges; a little water can then be added to just dissolve these crystals.

Estimation of the Iridium.—As to the double nitrites of rhodium and iridium formed with the potassium, they are not well adapted to the estimation of these two metals, inasmuch as they are more difficult to decompose with hot hydrochloric acid; and, further, the double chlorides thus obtained are very slightly soluble. Therefore, when it is a question of estimating iridium, it is necessary to divide into two parts the solution from which the osmium and ruthenium have been driven off. The first part should be treated, as has already been described, by KCl for the estimation of the platinum; the second part should be treated with NH_4Cl .

The double nitrite of ammonium and rhodium, as well as that of ammonium and iridium, are transformed, on the other hand, much more easily by aqua regia containing only a little nitric acid, into Rh_2Cl_6 and IrCl_4 . The iridium is precipitated in the form of chloroiridate by NH_4Cl , with which the solution should be saturated; this precipitate is collected on a filter, washed with a solution of NH_4Cl , and calcined. The metal is then reduced by hydrogen and weighed.

We could also precipitate the IrCl_4 by KCl in the state of chloroiridate, $\text{IrCl}_4 \cdot 2\text{KCl}$, by saturating the solution with KCl. By adding to the solution a little chlorine water, which does not act on the KCl as on NH_4Cl , the precipitation is more rapid. The product of the reduction is washed with water, to remove the chloride of potassium, and dried at 105° .

This method, when carried out as described, is fairly rapid. It is as well to operate on at least 5 grms. of mineral for each assay.

While the general method of M. E. Leidié gives all the iridium contained in the ore or in the residues, in whatever state it may exist, the present method will not give the iridium which is present in the form of osmide of iridium, as this latter is insoluble in aqua regia. It gives the iridium alloyed with the other metals; we know, in fact, that when it is in the form of an alloy, iridium is soluble in aqua regia, and in ordinary ores it is not found in the free state in sufficiently large quantities to remain undissolved.

The extraction of the iridium from osmide of iridium is, commercially, the subject of a special operation, entirely different from the extraction of iridium from platinum ores.

We propose to apply this modification of the original method to the commercial extraction of platinum and iridium, and to work out the practical and economic conditions of this application.—*Bull. Soc. Chim.*, Series 3, xxv., No. 18.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1901.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER "On the Variation with Temperature of the Thermoelectromotive Force and of the Electric Resistance of Nickel, Iron, and Copper between the Temperatures of -200° and $+1050^\circ$ " was read by Mr. E. P. HARRISON.

In this paper the changes with temperature of the thermoelectric force and the resistance of nickel and iron are traced over a wide range, and the singularities present in the curves representing these changes are investigated. In all experiments the same specimens of metal were used. Previous work on this subject has been performed by Tait, Fleming and Dewar, Holborn and Day, and Stansfield. In the author's experiments on E.M.F. an ordinary potentiometer method was used, the potential difference due to the thermo-couple being balanced against a portion of

that due to two accumulators. Before each reading a standard cadmium cell was balanced on a definite resistance in the accumulator circuit. Readings of E.M.F. of copper-nickel couples were accurate to 1.8 microvolts, while those of copper-iron couples were accurate to less than one microvolt at moderate temperatures. The heating arrangement was designed to give a uniform temperature which was measured by a platinum thermometer, and recorded automatically by Callendar's recorder. The cold junctions were placed in a large test-tube full of water; the test-tube was placed in a larger vessel also containing water. The temperature of the cold junctions varied with that of the room, and all observations were reduced to cold junction 0°C . Finally, in each case, observations were taken by placing the junctions in liquid air with the platinum thermometer beside them. To prevent oxidation of the metals forming the junctions at temperatures above 500° it was necessary to exhaust the porcelain tubes which contained them. The curves for variation of E.M.F. with temperature of copper-nickel and copper-iron couples are roughly a straight line and a parabola respectively. The differences between the actual curves and a selected straight line in the former case and a parabola in the latter case have been plotted against temperature. These difference curves show that the maximum variations occur in the case of copper-iron, at 70° , 230° , and 370° . The temperature of inversion (cold junction 0°C .) is 536°C ., and the neutral point is 262°C . In the case of copper-nickel maximum variations occur at 70° and 340° , and there appears to be a small hysteresis effect at the latter point. The temperature of inversion does not occur within the limits of the experiments, and there is no neutral point. The E.M.F. curve for a nickel-iron couple up to 700° has been obtained from the two previous experimental curves by addition. Above this temperature direct observations have been taken. This curve is nearly linear up to 900° , at which point a decrease in E.M.F. occurs. Curves of thermoelectric power have been derived from the E.M.F. curves by drawing tangents, and these show that a considerable range of the copper-iron curve can be represented by straight lines, but that the remainder is approximately parabolic. The copper-nickel power curve can be represented by bits of straight lines. The Peltier-coefficient variation curve for iron-copper is at first parabolic, and can then be made up of straight lines; for copper-nickel it can be made up of bits of parabolas. Considerable difficulty was experienced at high temperatures in getting concordant results owing to chemical changes and other effects. The experiments were therefore carried out under different conditions, and the results are discussed in the paper.

In the resistance experiments a potentiometer was employed, a manganin resistance coil immersed in an oil-bath being used as a standard. The resistance of nickel increases with temperature almost parabolically up to 370° , when a change of slope occurs, and the resistance increases much less rapidly and almost linearly up to 1050° . In the case of iron, the resistance curve does not change its parabolic form till nearly 800° , when it becomes linear, and remains so up to 1050° . The author concludes from his paper that the thermoelectric change in nickel-copper coincides approximately with the resistance change, but that no thermoelectric peculiarity exists for iron-copper at the temperature of the iron resistance change.

Mr. A. CAMPBELL said that with purer iron the change in thermoelectric properties might correspond with the change in resistance. Dr. Knott had performed experiments on nickel in 1886, and got results similar to those of the author. His results with thick wires were different to those with thin, probably because he did not exclude air and prevent oxidation. Mr. Campbell said that he had himself made experiments upon two samples of nickel differing in resistivity, and although their temperature coefficients were also different, the change in slope of the curve connecting resistance and temperature occurred at practically the same temperature in both specimens.

Their thermoelectric powers were identical up to 300°, but above they differed slightly.

Dr. D. K. MORRIS pointed out that the thermoelectric force, the resistance, and the magnetic properties should be observed at the same time. In taking a thermoelectromotive force there must be a temperature gradient, and in the interesting parts of the curves differences of magnetic properties may arise and produce discrepancies. He drew attention to the caution which must be exercised in differentiating by drawing tangents except when the curves are smooth. Dr. Morris said the connection between resistance and magnetic qualities was interesting. The temperature coefficient of resistance of a magnetic body rises with temperature so long as the body is magnetic, but reverses when the body becomes non-magnetic. He asked for information on the subject.

Prof. H. L. CALLENDAR said he had followed the research with interest, and referred to the experimental difficulties, especially at high temperatures. He should like to have said something in reply to Dr. Morris, but he was afraid the subject was a large one, and might well be discussed at some future meeting. There were several points to clear up, and the fact that the curves described cannot be represented by straight lines or parabolas showed that the subject was beyond the range of a simple theory.

The CHAIRMAN suggested that it might be well to re-examine more carefully some of the curves which are accepted as straight lines, and on which there is no complication due to magnetic properties. He hoped the author and others would continue working at this subject.

Mr. E. P. HARRISON, in reply to Dr. Morris, said he thought the number and accuracy of his observations justified him in drawing tangents to form his power and Peltier effect curves.

A paper on "*Asymmetry of the Zeeman Effect*," by Mr. G. W. WALKER, was read by the Secretary.

Professor Voigt predicted an asymmetry of the normal triplet, which has been verified by Zeeman. The author has considered the subject mathematically, and finds that asymmetry may arise as a second order term due to the magnetic field. The asymmetry would be more distinct the greater the field, which is opposed to the theory of Voigt. By giving numerical values to the symbols it is shown that the effect is extremely small. The author points out that his theory can provide an explanation of why a line may not be resolvable.

The Society then adjourned until November 8th, 1901.

NOTICES OF BOOKS.

Smokeless Powder, Nitrocellulose, and Theory of the Cellulose Molecule. By JOHN B. BERNADOU. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1901. viii.—200 pp. 12mo.

THE author and compiler of this neat volume is a lieutenant in the United States Navy, and dates the preface on board the U.S.S. "Dixie." He has brought together for the purpose of comparative study several essays by distinguished authors; to wit:—Two papers on "The Nitration of Cotton," by M. Vieille and by M. Bruley; "Pyrocollodion Smokeless Powders," by D. Mendeleeff; and the "Development of Smokeless Powder," by the author of the work. These are prefixed by original chapters on the theory of the cellulose molecule, and earlier views as to the composition and constitution of nitrocellulose, as well as a very clear presentation of the origin, nomenclature, and definitions of the diverse bodies of the nature of explosives used in military operations.

Lieutenant Bernadou has himself pursued chemical and military (or naval) researches for many years, and embodies in his treatise the results which confirm those of others, and at the same time throw much light on

them, showing their interdependence. His experiments conducted at the Naval Torpedo Station, Newport, resulted in the preparation of a new form of nitrocellulose capable of being converted directly by colloidalisation into a smokeless powder suitable for arms of all calibres. This is now manufactured on a commercial scale in several establishments. And one of the objects of the book announced by the author is to prepare the way for the introduction of future improvements in progressive explosives.

Besides the chemical side of the question, the author treats of the ballistic values and properties of the products.

The volume can be commended to students of military and naval problems involving the use of explosives.

H. C. B.

A Short Manual of Inorganic Chemistry. By A. DUPRÉ, Ph.D., F.R.S., &c., and H. WILSON HAKE, Ph.D., F.C.S., &c. Third Edition. London: Charles Griffin and Co., Limited. 1901. Pp. 391.

THIS new edition of the "*Manual of Inorganic Chemistry*," while retaining the main features of the preceding editions, has been at the same time thoroughly revised and partly re-written with special reference to the periodic law.

It is of importance that a student who has no previous knowledge of chemistry should be first grounded in the general principles which govern that science; with this object in view the authors have dealt, in the introductory portion of the book, with these general principles, and it is intended and hoped that this part should be read straight through before proceeding to the description of the properties of the various elements and their compounds.

The "*Scheme of Properties*" (p. 101) has been adhered to for the systematic and uniform arrangement of facts relating to the various elements and compounds. This scheme has been found to be of great convenience, and is already becoming well known.

The chapter on the "*Periodic Law*" goes very fully into the history and development of the scheme devised by Mendeleeff, though the atomic weights used by Mendeleeff do not always agree with the exact figures used in the text of this work.

In the second part of the book, "*Some Typical Elements and their Compounds*," a certain number of elements are first dealt with and fully described; they are then all considered *seriatim*, in the group arrangement laid down by Mendeleeff; this comprises eight groups, followed by the transition elements of Group I., viz., Cu, Ag, and Au.

We would, however, point out to the authors that, valuable and important as Mendeleeff's arrangement is, other more modern and more comprehensive arrangements have since been published, and we should at least expect them to be mentioned in a work that claims to be "thoroughly revised and partly re-written, with special reference to the periodic law."

The appendix contains some useful tables and additions, such as a paragraph on Gay-Lussac's "Law of Volumes," which should have been inserted in Chapter X., but was accidentally omitted. There are also Tables of the Thermal Values of Typical Chemical Reactions, the Heat of Neutralisation of some Acids and Bases, the Relative Avidity of Acids, &c. There is a full table of contents, and a good index of twenty-six columns.

Select Methods in Food Analysis. By HENRY LEFFMANN, A.M., M.D., and WILLIAM BEAM, A.M., M.D. With fifty-three Illustrations in the text, four full-page Plates, and many Tables. Philadelphia: P. Blakiston's Son and Co. 1901. Pp. 383.

As a concise summary of analytical methods for the use of both practical analysts and students this volume cannot fail to be of great value.

Great strides have been made in food analysis during

the past ten or fifteen years, but much of this information has been published unsystematically in reports and isolated papers, &c.

In the present work the authors have collected and arranged these methods as far as possible, including many of the most recent processes and results.

The effects of food adulteration and the methods of controlling it have not been given any consideration, as these topics do not appear to concern the analyst, but special attention has been given to the detection of preservatives, artificial colours, and poisonous metals.

The first and shorter part of the book deals with general analytical methods, such as specific gravity, boiling-points, polarimetry, microscopy, &c., with a short description of the apparatus and chemicals used. The second part on "Applied Analysis" contains, first, the general methods to be adopted, such as those for detecting poisonous metals, colours, &c., followed by a large section devoted to special methods of food analysis; these include methods for the analysis of starchy matters, fats and oils, milk and milk products, non-alcoholic beverages, such as tea, coffee, and cocoa, condiments and spices, alcoholic beverages, and flesh foods, including meat extracts.

The appendix contains some useful tables, and is followed by four full-page plates, two of which illustrate the appearance of various substances under the microscope, such as arrowroot, wheat, pea, rice, maize, ginger, buckwheat, &c.; while in the other two we have illustrations of the genuine tea-leaf (*Thea chinensis*), and twenty-one other kinds of leaf which are mixed with it for purposes of adulteration.

The book is well written, printed, and bound, and contains a comprehensive table of contents as well as a good index.

CORRESPONDENCE.

ON THE EXISTENCE OF A NEW ELEMENT ASSOCIATED WITH THORIUM.

To the Editor of the Chemical News.

SIR,—The last two numbers of the CHEMICAL NEWS (October 11th and 18th) contain a paper by Mr. Charles Baskerville "On the Existence of a New Element Associated with Thorium." The author says in a footnote that he wrote to me of his observations during the fall of the last year, and that he was surprised to observe in the *Proc. Chem. Soc.* of April 10th my article in which I give good evidence of the complexity of thorium, dividing that element into Th_a and Th_b .

Mr. Baskerville's letter really reached me in February, 1901, and it contains the following passage:—

"I may say I think that I have broken thorium up into two elements, but this may turn out in the end like so many other efforts to decompose many of our well known elements."

Absolutely no word more is said on the method used or the results obtained.

I confess myself guilty of not having answered this letter, at the receipt of which I could not but feel "*Noli turbare circulos meos!*" Perhaps an explanation may be found in the circumstance that at that very time I was engaged in reviewing the results of my work on the complex nature of thorium, which had occupied me during the last five years,* and of a work on some other rare earth metals, in order to communicate it to the Chemical Society; this was done in an exceedingly condensed form in March, 1901.

I would beg those chemists who are interested in this question to kindly compare the above quoted passage of

* The first facts pointing undoubtedly to the complex nature of thorium were found by me at the beginning of 1896.

Mr. Baskerville's letter with my condensed note on the subject in the *Proc. Chem. Soc.* (1901, p. 67), in order to decide whether that letter could have had any influence upon the results of my work. It will be seen further from my full paper on this exceedingly difficult subject which will appear in the *Transactions of the Chemical Society*, whether Mr. Baskerville or whether the writer is nearer the truth, and which of us two has the right of claiming priority of the discovery of the complex nature of thorium.—I am, &c.,

BOHUSLAV BRAUNER.

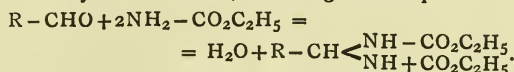
Bohemian University, Prague.
October 22, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

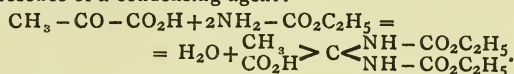
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 15, October 7, 1901.

ADDITION OF Urethane on Pyruvic Acid.—L. J. Simon.—Urethane is condensed by aldehydes, especially in presence of hydrochloric acid, according to the equation—

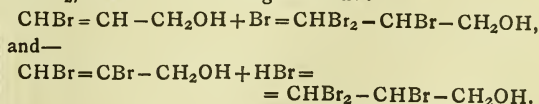


Pyruvic acid combines with urethane directly, without the presence of a condensing agent:—



The substance formed, diurethane pyruvic acid, can be clearly distinguished from pyruvic acid itself by a number of reactions. It is a white crystalline body, melting at 138–139°. It is non-volatile, but when heated strongly it decomposes, urethane distilling off. It is very soluble in hot or cold alcohol, also in acetone and chloroform, very slightly soluble in cold water, but soluble in hot water, with decomposition into urethane and pyruvic acid.

Bromated Malonic Dialdehyde.—R. Lespieau.—The author fixed hydrobromic acid on to propionic acid, and obtained a well characterised acid melting at 115°. He tried various experiments with this substance in the attempt to transform it into its isomer, but without success. He then further investigated the groups of atoms, $\text{C}_3\text{H}_5\text{BrO}_2$, and thought that the so-called acid might be the dialdehyde $\text{CHO}.\text{CHBr}.\text{CHO}$. He experimented on this substance, preparing its potassium derivative and testing its reactions with phenylhydrazine, and finally confirmed his hypothesis. Amongst the accessory products to this reaction he found the acid $\text{CHBr}=\text{CBr}-\text{CO}_2\text{H}$, melting at 85°, and also that the dibromated ether, $\text{CHBr}=\text{CR}-\text{CO}_2\text{H}$, can be replaced by the alcohol, $\text{CHBr}=\text{CH}-\text{CH}_2\text{OH}$, or by its methylic ether. The author has not yet satisfactorily explained the mechanism of these reactions. The formation of a primary aldehydic group by the action of bromine on an alcohol or an ether oxide is normal; that of the secondary group results probably from the intermediate production of a group, CHBr_2 , due to the following reactions:—



Reducing Properties of certain Nitric Ethers.—L. Vignon and F. Gerin.—During a study of oxycelluloses one of the authors showed that the nitrocelluloses possess reducing properties. These results have been confirmed

by other chemists. Nitromannite possesses the same reducing properties with regard to cupropotassic solution. The authors now investigate the properties of other nitric ethers to find a repetition of this characteristic. To this end they prepare the nitric derivatives of different mono- and polyatomic alcohols. Their results are shown in the following table.—

Nitric derivatives of:—	Reducing power with regard to cupropotassic solutions.
Methylic alcohol	None.
Ethylic alcohol	None.
Glycol (di)	None.
Glycerin (tri)	None.
Erythrite (tetra)	Slight.
Dulcitol (hexa)	Strong.
Mannite (hexa)	Strong.
Mannite (penta)	Strong.

From this table it appears that, starting from those of a certain atomicity, the nitrated derivatives of alcohols possess a special and characteristic reducing power with regard to cupropotassic solution.

MISCELLANEOUS.

Royal Institution.—The Christmas Course of Six Lectures to Young People, at the Royal Institution, will this year be delivered by Professor J. A. Fleming, F.R.S., Professor of Electrical Engineering in University College, London. His subject is "Waves and Ripples in Water, Air, and Æther," and the first lecture will be delivered on Saturday Afternoon, December 28, at Three o'clock. The remaining lectures on December 31, 1901, January 2, 4, 7, and 9, 1902.

The Fermentation of Cellulose.—V. Omeliansky.—The author has isolated and here describes a micro-organism capable of causing the fermentation of cellulose. This bacillus, *Fermentationis cellulosa*, is anaerobic, and belongs to the widely-spread group of butyric ferments. About 70 per cent of the decomposed cellulose is transformed into fatty acids (acetic and butyric), while 30 per cent is transformed into hydrogen and carbonic acid. This fermentation of cellulose differs essentially from the formic fermentation of the same substance; in fact, in this latter case, it forms only gaseous products—formene and carbonic acid.—*Arch. des Sc. Biol.*, vol. vii., p. 411.

The Oxidation of Hydroxylamine.—G. von Knorre and K. Arndt.—The authors have examined the action of various oxidising agents on hydroxylamine in aqueous solution. The apparatus used in these experiments is fully described in the original paper. It must not be forgotten that the hydrochlorate of hydroxylamine decomposes spontaneously as a result of the prolonged boiling of a solution of this salt. The gaseous products have been analysed by the eudiometric method previously described (*Berichte*, vol. xxxii., p. 2136); the excess of hydroxylamine was estimated by means of permanganate and ferric alum. The oxidising agents used are:—The alkaline nitrates in the presence of hydrochloric or sulphuric acid in variable quantities, hydrate of peroxide of manganese, permanganate of potash, chromosulphuric solution, vanadic acid, sulphate of copper, mercuric chloride, persulphate of ammonium, and peroxide of hydrogen. In nearly every case protoxide of nitrogen is principally formed, with a small quantity of binoxide, while the solution contains variable quantities of nitrous and nitric acids. In the case of vanadic acid alone, nitrogen is chiefly produced, with a small quantity of protoxide. Sulphate of copper gives pure protoxide if the hydroxylamine is in excess. Naturally, permanganate does not give any binoxide of nitrogen.—*Berichte*, xxxiii., pp. 30–42.

The Estimation of Copper in Biological Researches.—Ch. Dhéré.—To detect and estimate copper in organic liquors and tissues, M. Dhéré proposes to operate in the following manner:—The organic matter is destroyed by means of hot sulphuric acid, with the repeated addition of nitric acid to accelerate and complete the combustion. We thus obtain the copper in solution in the form of sulphate of copper. The dilute solution is electrolysed by means of a current of 2 to 5 volts (in the presence of a little nitric acid, which has the property of helping on the electrolysis), which is kept up until a freshly immersed portion of the electrode is no longer coated with copper. The weight of the copper deposited is found by weighing the electrode before and after the electrolysis. We can also estimate the copper by a colorimetric method. This is based on the possibility of estimating the amount of copper present in a solution by the intensity of the colouration produced under the action of ferrocyanide of potassium. In the present case the deposited copper is redissolved in nitric acid; the solution is then evaporated *in vacuo* over potash to drive off the whole of the free nitric acid which would otherwise interfere with the coloured reaction; the residue is taken up with water, and a 10 per cent solution of ferrocyanide of potassium added; the intensity of the colour is then estimated by bringing it to the same degree as that of a typical solution prepared with a titrated solution of copper. Under favourable circumstances 1/50th of a milligram of copper can be estimated.—*C. R. Soc. de Biol.*, 1900, p. 456.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "The Rapid and Approximate Estimation of Free Oxygen in Sewage Effluents and Waters," by Prof. W. Ramsay, F.R.S. "Phthalic Glycide," by Watson Smith. "Notes on the Manufacture of Varnish by the Pressure Process," by A. J. Smith.

WEDNESDAY, 6th.—Society of Public Analysts, 8. "The Composition of Milk," by H. Droop Richmond, F.I.C. "A Contribution to a Knowledge of the Chemistry of Cider," by Alfred H. Allen, F.I.C. "The Determination of Carbon in Steel by Direct Combustion," by Bertram Blount, F.I.C. "On Enteritis Sporogenes as Evidence of Sewage Pollution," by M. Dechan. Geological, 8.

THURSDAY, 7th.—Chemical, 8. "Note on the Non-existence of a Higher Oxide of Hydrogen than the Di-oxide," by W. Ramsay, F.R.S. "The Electrolytic Reduction of Nitrourea," by G. W. F. Holroyd. "The Constitution of Pilocarpine" (III.) and "A New Synthesis of α -Ethyl Tricarballic Acid," by H. A. D. Jowett. "The Action of Nitric Acid on Methyl Dimethylacetacetate," by W. H. Perkin, F.R.S. "An Incrustation from the Stone Gallery of St. Paul's Cathedral" and "Note on Asbestos," by E. G. Clayton. "Liquid Nitrogen Peroxide as a Solvent," by P. F. Frankland, F.R.S., and R. C. Farmer.

BIRKBECK INSTITUTION,

Breams Buildings, Chancery Lane, E.C.

DAY and EVENING CLASSES in SCIENCE.—CHEMISTRY, PHYSICS, GEOLOGY, METALLURGY, and ASSAYING. With Practical work in highly-equipped LABORATORIES.

Preparation for all the Examinations in Science for the University of London, Conjoint Board, and Pharmaceutical Society.

A Complete Course of Study in Theoretical and Practical METALLURGY and MINING.

Prospectus free. Calendar 6d. (post 8d.) on application.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2189.

SOME RELATIONS BETWEEN PHYSICAL CONSTANTS AND CONSTITUTION IN BENZENOID AMINES.*

PART III.

By W. R. HODGKINSON and L. LIMPACH.

IN the *Proc. Chem. Soc.*, 1893, ix., 41, we drew attention to some relationships between melting-points and constitution in some amines, and a further contribution by one of us and Gordan on the same subject appears in the *Trans. Chem. Soc.*, 1901, lxxix., 1080 (see also *CHEMICAL NEWS*, vol. lxxxiii., p. 297).

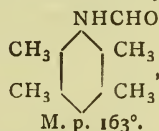
Since then, a considerable number of amines, their formyl and acetyl derivatives, have been prepared, it is believed in as pure a state as possible, and their melting-points, &c., determined.

Taking one particular series, the first point noticeable is that the difference between the melting-points of the formyl and acetyl derivatives of bases of the same constitution is the same, or very nearly so.

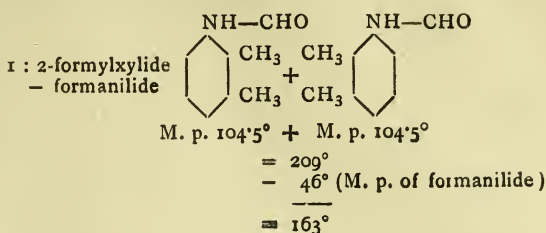
If in any base a methyl group be replaced by ethyl or oxymethyl, the melting-points of their formyl and acetyl compounds are changed. The differences, however, appear to be the same as between the formyl and acetyl derivatives of the methyl compounds. For instance, see Table I.

The tetramethyl bases exhibit some other peculiarities. As far as the melting-points of their formyl and acetyl derivatives are indications, they would appear to be built up of two xyldines less the melting-point of formanilide, &c. Thus, formyl aminotetramethylbenzenes—

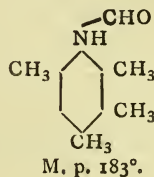
I.



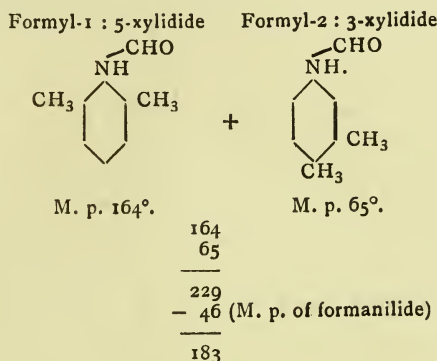
would appear to be composed of twice—



II.



composed of—



III.

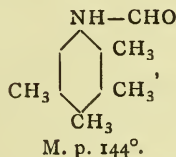
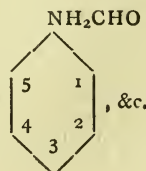


TABLE I.

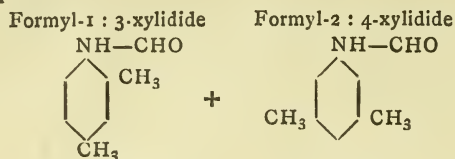
	Constitution (a).	M. p. formyl compound.	M. p. acetyl compound.	Difference.
Pseudocumidine	$\text{CH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 2 3 5	121°	164°	43
Ethylidimethyl aminobenzene	$\text{CH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 2 3 5	103°	145°	42
Paraxylylidine	$\text{CH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 1 4	116.5°	139°	22.5
Methyloxymethyl aminobenzene	$\text{OCH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 1 4	86°	109°	23
Cumidine	$\text{CH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 1 2 4	98°	126°	28
Oxymethyldimethyl aminobenzene	$\text{OCH}_3 \text{---} \text{C}_6\text{H}_2 \text{---} \text{CH}_3$ 1 2 4	68°	96°	28

(a) For simplicity, the constitution is represented on the plan



* Abstract of a Paper read before the British Association (Section B), Glasgow Meeting, 1901.

composed of—



M. p. 113°5'.

M. p. 76°5'.

$$\begin{array}{r} 113\cdot5 \\ 76\cdot5 \\ \hline 190\cdot0 \\ - 46 \quad (\text{M. p. of formanilide}) \\ \hline 144 \end{array}$$

ALUMINATE OF MAGNESIUM.

By EM. DUFAU.

THE use of the electric furnace enables us to obtain the mono-magnesian aluminate $\text{Al}_2\text{O}_4\text{Mg}$, or "spinel," with great ease.

The reproduction of this natural compound has been already effected by several chemists, viz., Ebelen, Daubrée, and Stanislas Meunier, but by the use of more complicated and much longer methods.

An intimate and well-calced mixture of 200 grms. of alumina and 100 grms. of magnesia is heated in a carbon crucible by means of an arc of 900 ampères and 45 volts. After heating for three minutes, we find in the crucible an entirely crystalline grey mass.

A portion of this mass is pulverised in an iron mortar and treated with hot nitric acid; thus we obtain a colourless crystalline powder mixed with numerous particles of carbon. To effect their separation we take advantage of their different densities, and by putting the powder into iodide of methylene, or into Klein's reagent, we can collect, at the bottom of the liquid, an absolutely homogeneous product which can be immediately submitted to analysis.

The substance is therefore finely powdered and treated in a platinum crucible with sulphate of potassium moistened with sulphuric acid, and then kept at a bright red heat until solution is complete. On cooling, the residue is taken up with water containing hydrochloric acid, and precipitated with a slight excess of ammonia; it is then left on the water-bath for some time, and the separated precipitate is re-dissolved in hydrochloric acid and re-precipitated with ammonia, &c.; this is repeated three or four times. Finally, the aluminium is collected and the magnesia precipitated in the filtrates in the form of ammonio-magnesian phosphate. The following are the figures thus obtained:—

	Found.	Calculated for $\text{Al}_2\text{O}_4\text{Mg}$.
Al_2O_3	72°72 and 72°43	71°68
MgO	27°43 „ 26°61	28°32

Aluminate of magnesium thus prepared appears in the form of colourless octahedra, it scratches quartz, has a density of 3·57 at 15°, is infusible before the blowpipe, and is only fusible in the electric furnace.

Hydrofluoric, hydrochloric, and sulphuric acids only attack it slowly; nitric acid has no effect. Fluorine has no action in the cold, but attacks it slowly when heated; chlorine, bromine, and iodine have no apparent action. Sulphur, at the temperature of melting glass, has only a very slight action. Carbon does not reduce this aluminate even at the temperature of the electric arc. Finally, however, alkalis in fusion, decompose it with facility, but their carbonates are without effect.

It is very easy to give to this aluminate of magnesium

the different colourations shown by the different varieties of spinel; it suffices to add to the reacting oxides 1 or 2 per cent of the oxides of iron, nickel, chromium, or cobalt, &c.; a rose-brown colour has been specially observed on adding oxide of copper.

We have endeavoured to obtain basic aluminates of magnesium, and have heated mixtures of two, three, and four molecules of magnesia for one of alumina, but we have never obtained anything but the mono-magnesian aluminate crystallised in the excess of fused magnesia.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 13.

THE UTILISATION OF FLUORIC GASES FORMED IN THE MANUFACTURE OF SUPERPHOSPHATES.

By C. ELSCHNER.

For some years past instructions have been given to inspectors of factories in Germany to prevent the direct escape into the air, from factory chimneys, of the fluoric gases which are given off during the solubilisation of phosphates. In a large number of factories of chemical manures, condensation apparatus by means of water vapour have been installed to retain the fluosilicic acid. Tarred wood chambers have been used with great success; these chambers are from 5 to 6 metres high, 5 to 6 metres long, and from 1 to 5 metres in width, divided into five compartments along their length by means of partitions. These partitions are pierced with holes alternately at the top and bottom, so that the current of gas is forced to traverse the whole length of each compartment. A Körtzing's apparatus made of hard rubber is placed in each compartment, and throws a fine spray of water in the opposite direction to that of the current of gas. Under the action of the water the fluoride of silicon is decomposed into fluosilicic acid, which is absorbed, and into gelatinous silica. The current of gas, almost entirely purified and freed from its acid constituents, is then allowed to escape up the chimney-shaft. The strongly acid liquor which collects at the bottom of the chambers is drawn into large tanks through leaden pipes. The liquor may then be neutralised with chalk and allowed to run off.

If, however, it is desired to treat these solutions specially it is preferable to keep the more concentrated liquors from the first and second compartments separate from the others; the former titrate up to 10 to 12° B. The liquor from the three other compartments, if too dilute to be of use, can be neutralised with chalk and run off.

To transform the liquor into fluosilicate of soda, it is treated, after filtration by the requisite quantity of a soda salt, such as a 10 per cent solution of sea-salt; it is then allowed to settle, and the precipitate is washed by decantation, passed through a filter-press, and dried. The precipitate can be completely separated and a pure product obtained, by using an excess of chloride of sodium, and constantly stirring the mixture while keeping the temperature at 15–25°.

However, the demand for fluosilicate of soda is not very considerable; it has therefore been found advisable to try and prepare other compounds from the fluorised gases. The fluates of Kessler were first thought of. As is well known, these are solutions of fluosilicate of magnesium and fluosilicate of aluminium, used for the hardening of calcareous stone.

Recently, attention has been drawn to the antiseptic properties of fluosilicic acid, and it has been recommended, amongst other uses, for preserving manures. As a matter of fact this acid appears to be much more efficacious than plaster, superphosphate of lime, or kainite for the preservation of farm-yard manure and for preventing the loss of nitrogen.

In every case the denitrifying action of certain bacteria is checked. On the other hand, however, the increasing

use of aqueous fluosilicic acid is interfered with by reason of the dislike most farmers have to having "bottles of acid" on their premises.

Attempts have been made to absorb the acid by infusorial earth or peat, but these products have not come into vogue.

A patent has recently been taken out for a new preservative for farm-yard manure; it consists of two pulverulent compounds, which have to be used together. One of them is prepared by absorbing as much sulphuric acid as possible by a powdered porous compound; the other is made by incorporating the solution of fluosilicic acid obtained from the first and second compartments of the absorption chambers with ground-up clay. The greater part of the acid combines with the bases contained in the clay. To preserve farm-yard manure one or two handfuls of each powder are strewn over it; by their mixture free fluosilicic acid is given off, and this acts as an antiseptic. This process is certainly an advance; it remains, however, to be seen at what prices these materials can be delivered by the makers. The second of these compounds might be prepared more economically by passing the gases directly over lime, well stirring the mixture, and drying the mass obtained. Instead of sulphuric acid incorporated with a porous body a powdered bisulphate might be employed with advantage. In this manner the antiseptic material would be obtained in a more concentrated form.—*Chemiker Zeitung*, 1900, p. 795.

EXTRACTION OF CYANIDES IN GAS-WORKS.

It is well known that among other impurities coal-gas contains sulphuretted hydrogen, ammonia, and hydrocyanic acid. Washing with water in conjunction with the ammonia in the gas does not suffice to extract this acid in the form of the easily soluble cyanide of ammonium, inasmuch as the carbonic acid, which is always present in the gas in excess, immediately decomposes the cyanide of ammonium formed, into carbonate and hydrocyanic acid. This explains why the ammoniacal waters from gas-works do not contain any cyanide of ammonium.

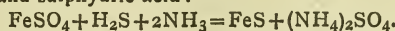
The small quantity of cyanide retained by these waters occurs in the form of sulphocyanide of ammonium, and a certain amount of cyanogen passes into the purifiers, when the following reaction takes place:—The cyanogen combines with the suboxide of iron, with the small quantity of ammonia still present, and with the sulphur compounds, forming insoluble ferro-cyanides and sulpho-cyanides, which gradually accumulate in the purifiers. Further, the whole of the cyanogen is not even then removed in this manner, but a very appreciable amount can be found in the gas delivered for consumption.

Up to 1880 the contents of the purifiers became a valueless product as far as the gas companies were concerned. The question has now taken, however, quite another aspect since the discovery of so many gold-mines, and the almost universal application, since this time, of the cyanide process of gold extraction. At the present time gas companies are making large profits from the spent contents of their purifiers.

It is, however, nevertheless true that this method of extraction of the cyanides leaves much to be desired. In the first place, the whole of the cyanogen is not recovered; again, it prevents the oxide from being entirely of use in removing the sulphuretted hydrogen; in this way it counteracts the original object of the purifiers.

The process devised by Dr. Bueb, and tried at the gas-works at Dessau, is possessed of great advantages, and deserves special mention, since it removes the whole of the cyanogen before the gas enters the purifiers. The principle is to conduct the gas, after leaving the Pelouze and Audouin condenser, into a special mechanical washer of the "Standard" type, consisting of four or five separate compartments, through which a solution of sulphate of iron

flows in the opposite direction to that of the current of gas. In the last compartment the concentrated, freshly-formed solution gives the following reaction in the presence of ammonia and sulphydric acid:—



Thus the sulphate of iron is transformed into sulphide of iron, and a solution of sulphate of ammonium is also formed. These liquors then pass into the next compartment, and there the ammonia and the cyanogen of the gas form, with the sulphide of iron, an insoluble double salt of cyanide of iron and ammonium, while the sulphuretted hydrogen being again set free is partially carried away with the gas, and partly forms sulphide of ammonium. This reaction continues in the other compartments up to the first where the gas enters, where it terminates.

The liquor, which is black in the first compartment, gradually becomes clearer, and is of a greenish-yellow colour in the last. The product leaves the cyanide washer in the form of a liquid mud, and contains 20 per cent of the yellow prussiate and 6 to 8 per cent of ammonia. This mud is boiled to drive off the ammonia, and passed through a filter-press; this finally gives a cake containing 30 per cent of blue and 44 per cent of yellow prussiate, and it is sold as such; to obtain 100 kilos. of prussian blue it is necessary to use 200 kilos. of sulphate of iron.—*Revue Generale des Sciences*, Year XII., No. 15, August 15, 1901.

SELENOCYANIC COMPOUNDS.

By W. MUTHMANN and E. SCHRÖDER.

Preparation of Selenocyanate of Potassium.—An intimate mixture of 70 grms. of pure KCy with 79 grms. of finely powdered commercial selenium is melted at as low a temperature as possible. Take up with 40 c.c. of water, and heat on the water-bath for three or four hours, renewing the water when necessary; then evaporate to dryness with constant stirring, and take up with 1 litre of boiling absolute alcohol; a current of CO₂ is then passed through the solution for two hours. Filter, drive off the alcohol by distillation, and dry the crystals of KCySe; the return should be from 96 to 98 per cent. In this manner all loss of selenium is avoided.

Preparation of Triselenide of Cyanogen.—Crystals of selenocyanate of potassium are placed in a flat bottomed vessel with one-third to one-half their weight of water, and a current of peroxide of nitrogen gas is passed over the mass, taking care to stir frequently, and to keep the temperature down to 0°. The mass first becomes red, and red crystals are formed having a blue metallic appearance by reflected light; these consist of C₃Se₄K, and have been described by Verneuil; they afterwards become yellow, and increase considerably in volume. Towards the middle of the operation it is as well to add, small quantities at a time, of fuming nitric acid; this causes the mass to become very frothy; C₂ and HCy are given off. When this reaction is terminated the residue is rapidly drained, then washed with very little water, and finally dried on porous plates in the desiccator. In this manner we obtain a mixture of nitre and triselenide of cyanogen, which is treated with boiling benzene to dissolve the latter. On cooling it is deposited in yellow flakes or needles. The product melts at 132°, forms a deep yellow liquid, and decomposes at 148.5°; when heated in a tube it gives a sublimate of selenium and SeO₂. It is perfectly insoluble in water, but is decomposed by it, forming Se and SeO₂. The best solvents are benzene and chloroform; it is slightly soluble in sulphide of carbon. Analysis and ebullioscopic examination give the formula C₂N₂Se₃.

Action of Triselenide of Cyanogen on some Organic Substances.—It has been seen that, in the case of certain bodies, such as CS₂, CHCl₃, CCl₄, this action is nil; on the other hand, it has been shown by Verneuil that there is a reaction and a deposit of selenium with alcohol and

ether. The same thing takes place if we rub up some of the triselenide with acetylacetic ether; selenium is deposited, and HCy given off. By distillation at 86–88° under 26 m.m. a yellow liquid with an acid reaction has been extracted; this liquid has a strong garlic odour, and contains selenium but no nitrogen. In the same way there is a reaction with acetone, but this is stopped when the acetone becomes saturated with the HCy produced. —*Berichte*, vol. xxxiii., p. 1765.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

THE work described in this article was undertaken with the object of finding out the most accurate and satisfactory method for the technical estimation of uranium.

The usual quantitative methods for the estimation of uranium were first repeated, then new methods for its separation and estimation were tried on solutions containing known amounts of pure salts, and the best conditions for both separation and determination were carefully worked out.

The research was drawn to a close by making a number of assays of uraninite, in which the results obtained from the work on pure salt solutions were applied. These assays tested the methods on the most important ore of uranium, and thus collected the data in the form of analytical methods.

Historical Introduction.

Uranium was discovered by M. H. Klaproth, who separated what he thought to be a new element from pitchblende—also known as uraninite—the principal ore of uranium. This was in 1789, and what he obtained was not the element, but its lower oxide, UO_2 . He named the element uranium in remembrance of the planet Uranus, which Herschel discovered in 1781.

From 1789 to 1795 much work was done on the investigation of uranium, but nothing new was discovered till 1840, when E. Péligot succeeded in isolating metallic uranium in powder form by heating uranous chloride (UCl_4) with metallic sodium (*Liebig's Ann. Chem.*, 1842, xli., 141). He made a great number of experiments, the results of which proved that what was previously thought to be the element uranium was its lower oxide (UO_2), which plays the part of a base, a true inorganic radical. This discovery seems to have been an impetus to the further study of this element, as we find records in the different journals, of the years that follow, of several of the eminent chemists of the day investigating uranium, and trying to find new methods for its estimation.

Clemens Zimmerman was the next chemist of note to investigate uranium. He studied methods for isolating the metal, and methods for its estimation and separation from other elements, and prepared many of its salts, studying their chemical and physical properties (*Liebig's Ann. Chem.*, vols. cxix., cciv., ccxiii., and ccxiv.). This work covered a number of years, from 1877 to 1884. So 1877 marks the second revival of interest in the element uranium. The first revival was in 1840, when Péligot isolated metallic uranium. The third revival is the present time, brought on by the great industrial demand for uranium ores.

In 1854 the only use to which uranium was put was for making a very fine black for porcelain painting (Whitney's "Mineral Wealth of the United States"), and from 1850 to 1866 it was much used in photography. At present its uses are for the preparation of acetate and nitrate salts (which are used as chemical reagents), for the manufacture

of a certain highly prized canary-yellow coloured glass, for the preparation of a pigment used for porcelain painting, and, lastly, for making a steel which has properties superior to nickel steel (*Moniteur Industriel*, 1900, xxvii., 44).

PART I.—SEPARATION OF URANIUM.

Separation of Uranium from Members of the Fifth and Sixth Group.

The only point to be determined for the well-known separation by hydrogen sulphide was the exact acidity of the solution. This was done by mixing standardised solutions of lead, copper, and uranium in different proportions, and precipitating the lead and copper by hydrogen sulphide, under varying conditions of acidity and temperature. The experiments were all conducted quantitatively. These showed that a perfect separation was effected when 1 c.c. of concentrated nitric acid (sp. gr. 1.42) was present to every 50 c.c. of solution, and the solution saturated with hydrogen sulphide in the cold.

With hydrochloric acid, 1 c.c. of concentrated acid (sp. gr. 1.20) to 50 c.c. of solution gave excellent results. This amount must not be exceeded, as when 2.5 per cent of concentrated acid was present the precipitation of the lead was incomplete. Less acid must be present if the precipitation is done from a hot solution, but this is not recommended.

As 5 c.c. of concentrated acid in a bulk of 250 c.c. solution gave a perfect separation of uranium from the metals of the fifth group, whose sulphides are the most soluble—lead and cadmium—and also from copper, these conditions must also be suitable for the other members of this group. Lead requires the least amount of free acid to retain it in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, and silver (Fresenius's "Quantitative Chemical Analysis," 1900, p. 456).

Separation of Vanadium from Uranium.

Vanadium is one of the common associates of uranium, and especially so in the minerals which occur in Colorado. Carnotite, the most common of these minerals, has of late reached commercial importance.

The separation of vanadium from uranium presents very little difficulty unless phosphoric acid is present, in which case the separation is troublesome. Friedel and Cumenge (*Amer. Journ. Sci.*, 1900, x., 135) separated vanadium from uranium by evaporating the solution to dryness with nitric acid. The uranium was then extracted from the dry mass with a warm dilute solution of ammonium nitrate. For this separation, no phosphoric acid should be present as it renders the uranium oxide, with which it is combined, insoluble in the dilute ammonium nitrate solution.

The method for the separation of vanadium from iron by means of mercuric oxide and mercurous nitrate (Blair's "Chemical Analysis of Iron," Third Edition, p. 200), has been used with success by A. C. Langmuir, for the separation of vanadium from uranium in the analysis of carnotite (see Paper read before New York Section of American Chemical Society, at March meeting). The finely divided mineral was dissolved in the smallest possible amount of nitric acid, and the silica filtered off. The solution was diluted to about 500 c.c., and the vanadium precipitated by means of mercurous nitrate as follows:—The nitric acid solution was nearly neutralised with pure yellow mercuric oxide, and the vanadium then precipitated by the addition of a strong solution of mercurous nitrate. The solution was brought to boiling, after which it was filtered. (If chromium, tungsten, or molybdenum are present they go down as mercurous salts with the mercurous vanadate). The precipitate was washed with a warm dilute solution of mercurous nitrate, after which it was dried, ignited, and weighed as V_2O_5 . The excess of mercury in the filtrate was removed by means of hydrogen sulphide gas. After expelling the hydrogen sulphide from the filtrate by slow boiling, the uranium was determined by the ordinary method.

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxi., No. 10.

O. P. Fritchle's Method (*Eng. Min. Journ.*, Nov. 10, 1900; *CHEM. NEWS*, 1900, lxxxii., 258) is said to be particularly adapted to the mineral carnotite. The finely divided mineral was decomposed at boiling temperature with 10 c.c. nitric acid, taken up with 10 c.c. water, neutralised with a saturated solution of sodium carbonate, added 5 c.c. in excess, and 20 c.c. of a 20 per cent sodium hydroxide solution; it was boiled slowly for half-an-hour, and the precipitate allowed to settle. The vanadium, uranium, and iron were all precipitated by the sodium carbonate, but on adding a moderate excess and a large excess of sodium hydroxide, the vanadium was dissolved while the uranium and iron remained insoluble. Uranium is easily precipitated by sodium carbonate and sodium hydroxide in the presence of an iron salt. The precipitate was washed with a solution of sodium hydroxide. The uranium and iron were then separated by the ordinary method, and each determined volumetrically by means of standard permanganate, after reducing their sulphate solutions at boiling temperature with metallic aluminium.

Separation of Uranium from Members of the Third and Fourth Groups, particularly Iron.

The methods ordinarily used for separating uranium from the other members of the fourth group and those of the third group depends on the solubility of uranium hydroxide and sulphide in an excess of a strong solution of an alkali carbonate. The hydroxides and sulphides of the other members of these two groups are, with the exception of iron and nickel, insoluble in alkali carbonate solutions. The hydroxides of these two metals are only slightly soluble in strong alkali carbonate solutions; in cold dilute solutions they are almost insoluble.

The element which gives the most trouble in effecting a separation from uranium is iron. A great number of methods have been proposed, of which the best known are Pisani's ammonium carbonate (*Comptes Rendus*, lii., 106), and Patera's sodium carbonate methods (*Zeit. Anal. Chem.*, 1866, v., 228), neither of which are very satisfactory. Rose used ammonium carbonate followed by ammonium sulphide (*Zeit. Anal. Chem.*, 1862, i., 410), thus precipitating the iron. This latter method is far from satisfactory, especially if the uranium is small in amount. Rheineck's basic acetate method (*CHEM. NEWS*, 1871, xxiv., 233) has been used with success when the uranium was present in considerable quantity.

Ether Separation.—The use of ether to effect a separation of iron from uranium was suggested by A. C. Langmuir in a recent article on the analysis of nickel ores (*Journ. Amer. Chem. Soc.*, 1900, xxii., 102). He found that iron could be separated from copper, manganese, aluminum, cobalt, nickel, and zinc, by taking advantage of the solubility of ferric chloride in ether free from alcohol. The chlorides of the other metals are not taken up by the ether, but remain in the aqueous hydrochloric acid solution. When iron is in the ferrous condition, Rothe (*CHEM. NEWS*, lxi., 182) found that it was not taken into solution by the ether, but remained with the other metals in the aqueous solution. So it is necessary to oxidise the iron before attempting to make the separation.

Experimental.

The separation of iron from uranium by means of ether was tried, and, as the result, a clean and rather rapid separation has been worked out. This separation depends on the complete extraction of ferric chloride (in an aqueous hydrochloric acid solution) by ether which is free from alcohol, and the retention of uranyl chloride in the aqueous hydrochloric acid solution.

Before undertaking the separation of iron from uranium by means of ether, two solutions containing uranium alone were treated three times with ether, as described in the following experiments, in order to test the solubility of uranyl chloride in ether. These experiments showed uranyl chloride to be entirely insoluble in ethyl ether which is free from alcohol.

The experiments which follow were made with solutions containing both uranium and iron. Measured amounts of a standard uranium nitrate solution and of a standard ferric chloride solution were placed in a small beaker, and the solution twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass was taken up with about 10 c.c. dilute hydrochloric acid (sp. gr. 1.10), and heated till all salts were dissolved, but not long enough to lose any of the acid by volatilisation. After the solution had cooled, it was poured into a 250 c.c. separatory funnel, and the beaker rinsed out with dilute hydrochloric acid (sp. gr. 1.10). The rinsings were added to the separatory funnel till the volume of the solution had reached 50 c.c. Fifty c.c. of ether, free from alcohol, and previously shaken up with hydrochloric acid (sp. gr. 1.10), were added and agitated for about ten minutes, occasionally relieving the pressure in the funnel. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid solution of uranyl chloride, containing some iron, was drawn off, catching it in another separatory funnel. The ether solution of ferric chloride was washed twice with 10 c.c. dilute hydrochloric acid (sp. gr. 1.10), and the washings, after allowing to separate, were run into the funnel containing the uranium.

On determining the amount of iron extracted from the hydrochloric acid solution by the ether, it was found that all the iron was not separated from the uranium by one extraction, about 10.5 per cent of the amount taken remaining in the aqueous solution with the uranium.

On finding that all of the iron was not separated from the uranium by one "ether extraction," two extractions were made on a solution containing 0.1155 gm. uranium, and 0.0901 gm. of iron. The first extraction was made in the same manner as outlined above, and the second as follows:—The solution in the lower separatory funnel was again shaken for about seven minutes with 50 c.c. ether. After thoroughly shaking together, the two solutions were allowed to separate, and the lower aqueous hydrochloric acid layer run into a second funnel. The ether solution was twice washed with 10 c.c. hydrochloric acid (sp. gr. 1.10), and the washings caught in the second funnel. The ether solution was run into a beaker which contained the ether from the first extraction. After distilling off the ether, the iron was determined by titration with 0.1 normal potassium permanganate solution. About 3.5 per cent of the iron taken remained in the aqueous solution with the uranium.

The next five separations of iron from uranium were made by using hydrochloric acid of about 1.10 specific gravity (1 part acid, sp. gr. 1.20, and 1 part distilled water). In all cases three "ether extractions" were made, whereby practically complete separations of iron from uranium were obtained. The solutions contained from 0.0901 to 0.1802 gm. iron, and from 0.0962 to 0.2310 gm. uranium. The amount of metal in their respective solutions was determined volumetrically, and did not vary more than 0.3 per cent of the theoretical amounts taken.

The next five experiments were made by varying the strength of the hydrochloric acid used. The procedure was the same as above, making three extractions with ether. For the first three solutions, hydrochloric acid of about 1.133 specific gravity (2 parts acid, sp. gr. 1.20, and 1 part distilled water) was used; and for the last two solutions hydrochloric acid of about 1.066 specific gravity (1 part acid, sp. gr. 1.20, and 2 parts distilled water). The separation in both cases, of iron from uranium, was incomplete. When hydrochloric acid of 1.133 specific gravity was used the amount of iron remaining with the uranium, after three "ether extractions," was about 6 per cent of the amount taken. With hydrochloric acid of 1.066 specific gravity, the amount of iron which remained with the uranium after three "ether extractions," was about 25 per cent of the amount taken.

The most complete separations of iron from uranium by means of ether are evidently obtained by using hydrochloric acid of 1.10 specific gravity. This is the same

TABLE I.—Separation of Iron from Uranium by Extraction with Ether.

Expt. No.	Specific gravity of HCl used.	Volume of sol. at first extraction. C.c.	Number of ether extractions made.	Ether used for—			Theoretical amount of uranium taken.	Amount of uranium determined in aqueous HCl solution.	Theoretical amount of iron taken.	Amount of iron determined in ethereal extract.
				First extract'n. C.c.	Second extract'n. C.c.	Third extract'n. C.c.				
1.	1.10	40	3	50	40	40	0.09625	0.09588	—	—
2.	1.133	40	3	50	40	40	0.09625	0.09643	—	—
3.	1.10	50	1	50	—	—	0.11550	0.13171	0.09010	0.08415
4.	1.10	50	1	50	—	—	0.11550	0.14700	0.09010	0.07700
5.	1.10	50	2	50	50	—	0.11550	0.12466	0.09010	0.08690
6.	1.10	40	3	50	50	50	0.09625	0.09643	0.09010	0.08993
7.	1.10	25	3	75	50	35	0.11550	0.11525	0.09010	0.09020
8.	1.10	25	3	75	50	35	0.09625	0.09643	0.18021	0.18029
9.	1.10	25	3	75	50	35	0.19250	0.19228	0.09010	0.08993
10.	1.10	25	3	75	50	35	0.23099	0.23069	0.09010	0.09037
11.	1.133	40	3	50	50	50	0.09625	0.10584	0.09010	0.08663
12.	1.133	25	3	75	50	35	0.11550	0.12068	0.09010	0.08580
13.	1.133	25	3	75	50	35	0.19250	0.20815	0.09010	0.08250
14.	1.066	25	3	75	50	35	0.09625	0.20933	0.18022	0.12705
15.	1.066	25	3	75	50	35	0.23099	0.27224	0.09010	0.07150

strength as was found by Speller (CHEM. NEWS, 1901, lxxxiii., 124) to be the best for the separation of iron from copper, manganese, aluminum, chromium, cobalt, and nickel.

When rather concentrated hydrochloric acid (sp. gr. 1.133) was used for the solution of the chlorides of iron and uranium, it was noticed that on diluting the aqueous solution, after agitating with ether, quite an amount of ether separated. This seems to explain the reason why iron is not readily separated from uranium by means of ether when strong hydrochloric acid is used to bring their chlorides into solution, the iron being retained by the large quantity of ether which remains with the acid solution.

The results obtained are shown in Table I.

Separation of Uranium from Cobalt, Nickel, and Zinc.

Wolcott Gibbs separated uranium from cobalt, nickel, and zinc by means of hydrogen sulphide. He states that this method is much simpler than those ordinarily used, and also gave excellent results (Silliman's *Amer. Journ. Sci. and Arts*, 1865, [2], xxxix., 62). To the neutral or nearly neutral solution of the chlorides of uranium, cobalt, nickel, and zinc, add sodium acetate in excess, and a few drops of acetic acid. The solution is boiled, and a rapid current of hydrogen sulphide passed through the boiling solution for half-an-hour. Every trace of the cobalt, nickel, and zinc is precipitated as sulphides, while the whole of the uranium, and any manganese, if present, remains in the boiling solution. The precipitate is thrown on a ribbed filter, and quickly washed with cold hydrogen sulphide water. The precipitate is easily washed, and though the sulphides of cobalt and nickel formed in this manner are more easily oxidised than when precipitated by sodium sulphide from a boiling solution, they will be found to present no difficulty as regards oxidation upon the filter. If manganese is in the filtrate it may be determined by boiling with hydrochloric acid, and precipitating it in the usual manner with sodium carbonate. The uranium in the filtrate is determined by the ordinary method.

Rose separated uranium from cobalt, nickel, and zinc by means of barium carbonate (Rose's "Chimie Analytique—Analyse Quantitative," 1862, p. 248). The precipitation of the uranium is complete from uranic solutions which contain a small amount of free acid, either hydrochloric or nitric acid. Barium carbonate, which is diffused in water, is added in excess, and the solution allowed to stand twenty-four hours. The presence of ammonium chloride is necessary in order to keep the cobalt, nickel, and zinc in solution. The uranium is separated from the excess of barium carbonate by dissolving the precipitate in hydrochloric acid, and adding dilute sulphuric acid. The uranium in the filtrate is precipitated with ammonia,

and weighed as oxide. C. Rammelsberg (*Chem. Centrbl.*, 1884, p. 806) employed this method to separate uranium from cobalt and nickel, and obtained excellent results; but when manganese and zinc are present it cannot be advantageously employed.

(To be continued).

A NEW SOLUTION FOR THE COPPER VOLTAMETER.

By WILLIAM K. SHEPARD.

THE importance of the convenient and accurate method of measuring electric currents by the voltameter depends very largely upon the construction of a voltameter which admits of high current densities.

The silver voltameter gives results of a high degree of accuracy, but is not conveniently used except for small currents; the copper voltameter, however, from the cheapness of its materials, finds employment in the laboratory for the measurement of comparatively large currents.

As ordinarily used, the copper voltameter is subject to irregularities due to the solvent effect of the solution in some cases and the oxidation of the copper in others. The voltameter solution recently investigated by the writer commends itself by the facts that these irregularities are avoided, and that approximately twice the current density permissible with solutions hitherto in use may be employed without loss of accuracy, thus allowing large currents to be measured without inconveniently increasing the size of the electrolytic cell.

Many different solutions for the voltameter have been recommended by various experimenters. Gray (*Phil. Mag.*, 1886, xxii., p. 289), using a copper sulphate solution of density 1.15 to 1.18 with 1 per cent free sulphuric acid, found that the highest current density desirable was 0.02 ampère per square centimetre of cathode surface.

Vanni (*Wied. Ann.*, 1891, x., p. 214; and *Phil. Mag.*, 1888, xxv., p. 179) observed that a copper sulphate solution of density 1.12 with 1 per cent free sulphuric acid dissolved copper, and therefore gave indications always too small. With an increase of the current density the deduced electro-chemical equivalent of the copper increased. A solution neutralised with copper hydrate, on the contrary, yielded results in constant excess, probably on account of the oxidation of the copper. By adding to a litre of the normal solution $\frac{1}{3}$ gm. of a solution which contained 1 per cent sulphuric acid, he found neither a gain nor a loss in the weight of a piece of copper immersed in it. With this solution he successfully used a current density of 0.011 $\frac{\text{ampère}}{\text{c.m.}^2}$, but no experiments seem to have been made to determine the limit.

Cettel (*Chemische Zeitung*, 1893, p. 543) obtained smaller deposits of copper from copper sulphate solutions than Faraday's law demands resulting from the formation of oxygen compounds, such as HSO_4 . By the addition of alcohol, these losses were avoided. He advised as the best solution:—

150	grms.	CuSO_4
50	"	H_2SO_4
50	"	Alcohol
1000	"	H_2O

Beach (*Am. Journ. Sci.*, 1893, xlvii, p. 81) investigated the use of copper nitrate in the voltameter. His solution, after neutralisation, had a density of about 1.53, and contained one drop of a saturated solution of NH_4Cl to 100 c.c. of the nitrate. The NH_4Cl was added to prevent the oxidation and consequent excess of deposit which occurs when a neutral solution is used alone. He found that he could use a much higher current density with this solution than with the copper sulphate solutions commonly used. But as copper nitrate is relatively expensive in comparison with the sulphate, it is not so well suited for general laboratory use.

It seemed to the writer of interest to attempt the use of a neutral solution of the sulphate in the same manner, with the aim of increasing the allowable current density. The solution was prepared as follows:—A saturated solution of copper sulphate was boiled for a short time to expel the air, and then kept at 100°C . for about an hour in contact with metallic copper in order to neutralise the solution; the density was then about 1.20. A very small amount of NH_4Cl was added, about 0.05 of 1 per cent.

Two voltameters were used in the investigation. They were connected in series in order to see how the different solutions would agree when using exactly the same current. Each voltameter consisted of three anode and two cathode plates, the cathode plates being placed alternately between the anodes at distances of about 2 c.m. The plates were 10.5×19 c.m., of which a working cathode surface of about 600 c.m.² was employed. The voltameters were used in battery jars 20 c.m. high and 15 c.m. in diameter.

The method used in the preparation of the cathode plates was that given by Gray (*Phil. Mag.*, 1886, xxii.). The edges and corners were well rounded and the plates polished with sand-paper. They were next placed in water slightly acidulated with sulphuric acid for a short time to remove any trace of oxide, rinsed in clean water, dried with filter-paper and then over a gas flame. After copper had been deposited, the plates were not exposed to the air for a time longer than absolutely necessary before the copper sulphate solution had been completely washed off. The reason for this is that a copper plate oxidises rapidly when wet with a solution of neutral copper sulphate and exposed to the air. This was accomplished by removing the voltameter plates as a whole from the solution and dipping at once into water containing a few drops of sulphuric acid. They were then rinsed in clean water, dried with filter-paper and over a flame.

Gray's solution was first tried for comparison. Very good deposits were obtained using a current density up to about $0.03 \frac{\text{ampère}}{\text{c.m.}^2}$; but the deposits would sometimes

differ as much as 1 per cent in the two voltameters.

Cettel's solution gave fine deposits for low current densities. When, however, the current density was increased, the plates blackened badly, and copper was found in the form of powder on the bottom of the jars. The highest current density permissible with this solution was

$0.02 \frac{\text{ampère}}{\text{c.m.}^2}$.

Then the solution with NH_4Cl , prepared as above, was investigated in the same manner. For low current densities, it gave as good results as had been obtained with either Gray's or Cettel's solution, but, in contradistinction to these, the results continued to be satisfactory when

these limits were widely surpassed. With a current of 20 ampères the density was increased, by raising the plates so as to lessen the immersed surfaces, to a value even more than $0.05 \frac{\text{ampère}}{\text{c.m.}^2}$. Notwithstanding this very

material increase in the demands upon the voltameter, the deposits still remained perfectly satisfactory. With 30 ampères and a current density of $0.045 \frac{\text{ampère}}{\text{c.m.}^2}$ the

solution still gave results differing by less than 1 per cent.

The voltameters were then filled, one with Gray's or Cettel's solution, and the other with the new solution. When employed for low current densities, the solutions in all cases gave deposits agreeing within the limits of error imposed by the methods employed.

With regard to the constancy of the apparent electro-chemical equivalent when a high current density was used with this solution, no exact statement can be made, as the absolute measurement of the current was not attempted. In the first part of this investigation a Weston ampèremeter was included in the circuit, the error of which the writer has reason to believe was less than 1 per cent. Assuming the indications of this instrument to give the true values of the current, the electro-chemical equivalent obtained from the new solution was fairly constant.

The results are not given, as different values of the current being used they included the errors of the instrument.

Having now performed these preliminary experiments showing that the solution could be employed for large current densities without loss of accuracy, and having obtained a fair idea of the working of the solution, experiments were begun with the aim of eliminating the error of the instrument.

Another Weston ampèremeter was obtained which read only to 15 ampères, each ampère division being divided into ten parts. So that with this instrument the current could be measured with an error in the reading of less than one-fiftieth of an ampère. The instrument was not assumed to be correct, but after the experiments had been finished the results were averaged, and, taking the electro-chemical equivalent of copper to be $0.000329 \frac{\text{gm.}}{\text{ampère sec.}}$

the true value of the current at the division used on the instrument was obtained.

Only one point on the ampèremeter was used, namely, the one which gave the nearest value to 15 ampères. Thus, with the same division and changing the current density by raising the immersed surfaces of the voltameter plates, the error of the instrument was eliminated.

From what has just been said, it will be plain that the results given below are not presented as determinations of the electro-chemical equivalent of copper; the experimental data are reduced to that form simply for convenience in comparing them.

The current was obtained from a storage battery of 50 cells, and was kept constant by means of a copper sulphate resistance which could be varied at will by varying the distance between the copper plates.

An auxiliary circuit was arranged whose resistance was equal to that of the two voltameters. The current was thrown by means of a switch first through the auxiliary circuit to the ampèremeter and resistances included in the circuit. These were allowed to heat up until everything became constant, and the resistance adjusted so as to give the desired reading of the ampèremeter. Then the current was thrown through the voltameters, and assumed the desired value instantly.

The duration of an experiment was twenty minutes, so that a deposit of about 6 grms. was obtained. This deposit showed no oxidation, even up to the highest current density used, which was greater than $0.07 \frac{\text{ampère}}{\text{c.m.}^2}$.

The results are arranged in series according to their respective current densities, as follows:—

SERIES I.

Current Density = 0.02		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3287.2
2.		3295.0
3.		3288.4
4.		3288.9
5.		3292.8
6.		3297.2
7.		3286.8
8.		3288.4
9.		3293.9
10.		3289.4
11.		3287.2
12.		3293.4

The mean of these values is 3290.7, with a probable error of ± 2.4 for a single observation.

SERIES II.

Current Density = 0.03		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3288.4
2.		3291.7
3.		3296.7
4.		3291.7
5.		3292.8
6.		3288.3
7.		3295.5
8.		3295.9
9.		3294.4
10.		3287.2
11.		3288.4
12.		3288.9

The mean of these values is 3291.7, with a probable error of ± 2.3 for a single observation.

SERIES III.

Current Density 0.04		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3287.8
2.		3294.4
3.		3287.2
4.		3284.5
5.		3283.9
6.		3283.4
7.		3296.7
8.		3295.0
9.		3292.2
10.		3295.5
11.		3296.1
12.		3296.7

The mean of these values is 3291.1, with a probable error of ± 3.6 for a single observation.

SERIES IV.

Current Density 0.05		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3286.2
2.		3286.2
3.		3290.5
4.		3293.4
5.		3288.4
6.		3286.8
7.		3297.2
8.		3292.8
9.		3285.5
10.		3287.2
11.		3286.8
12.		3293.4

The mean of this series is 3289.5, with a probable error of ± 2.6 for a single observation.

SERIES V.

Current Density 0.06		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3288.4
2.		3294.4
3.		3287.2
4.		3290.0
5.		3292.8
6.		3290.5
7.		3291.7
8.		3295.0
9.		3283.9
10.		3287.2
11.		3287.2
12.		3291.1

The mean of these values is 3290.0, with a probable error of ± 2.2 for a single observation.

SERIES VI.

Current Density 0.07		ampère.
		c.m. ²
No.		Equivalent $\times 10^7$.
1.		3291.7
2.		3288.9
3.		3291.1
4.		3286.2
5.		3290.5
6.		3290.0
7.		3287.2
8.		3286.2
9.		3290.5
10.		3292.8
11.		3286.2
12.		3282.8
13.		3291.7
14.		3287.2
15.		3292.2
16.		3288.9

The mean of these values is 3289.0, with a probable error of ± 1.9 for a single observation.

The results are arranged for comparison in the following table:—

Series.	Current density.	Mean.	Probable error of mean.
I.	 0.02	3290.7	± 0.7
II.	 0.03	3291.7	± 0.7
III.	 0.04	3291.1	± 1.0
IV.	 0.05	3289.5	± 0.7
V.	 0.06	3290.0	± 0.6
VI.	 0.07	3289.0	± 0.6

These results show no dependence upon the current density. In fact, series VI., which differs most from the others, could be slightly increased for the following reason. The day after this series was taken the watch which had been used to measure the time was rated with a clock and found to be gaining at the rate of two seconds an hour when lying at the side of the ampère-meter. This was doubtless caused by the magnetic field of the ampère-meter, as the watch at other times was very correct.

If a connection were applied for this to series IV. it would increase it by about one part in 1800, so that it would become 3290.6, which is in still closer agreement. During series III., IV., V., which were taken after this fact had been discovered, the watch was rated and proper connections were applied. But as the watch had not been rated during series I., II., and VI., the corrections cannot be applied to them.

It is also proper to observe that although the current density was widely varied there is no loss of accuracy, as is shown by the probable errors of a single observation in the different series.

For current densities of $0.05 \frac{\text{ampère}}{\text{c.m.}^2}$ or greater the solution was found to heat a little during the first experiment. Results which were obtained during the rise in temperature of the solution were always slightly greater than those obtained after the solution had become warm and at a uniform temperature throughout. The unequal temperature of the solution may be avoided by stirring or by making a preliminary experiment to warm up the solution. The best way was found to heat the solution by means of a flame to a temperature of about 35 or 40°C . before making an experiment. The deposits were then found to be very satisfactory even up to a current density of over $0.07 \frac{\text{ampère}}{\text{c.m.}^2}$ and the resulting values of the equivalent to agree closely with those obtained with the low current densities.

The results given in series III., IV., V., and VI. were obtained with the solution at a temperature from 35 to 40°C ., while series I. and II. were obtained with the solution at the temperature of the room, about 20°C . We see therefore that the temperature from 20° to 40°C . has practically no influence upon the results given by the solution; but that any inequality in the temperature of the solution will cause slight errors, and therefore should be carefully avoided.

The same solution was used throughout the second part of this investigation. Perhaps fresh solutions would have given more consistent results, but certainly no large error is introduced by the repeated use of the solution.

We may collect the results with this solution as follows:—

The weight of copper deposited is practically independent of the temperature between 20° and 40°C .

The results are independent of the current density within the limits given.

The solution may be used a large number of times.

The solution may be used with a current density two or three times as great as that permissible with others commonly in use, so that to measure a given current a considerable smaller voltameter may be employed than with the older solutions.

Current-measuring instruments may be calibrated by its means with an error of only about one-tenth of one per cent.—*American Journal of Science*, [4], xii., No. 67.

NOTICES OF BOOKS.

Elementary Experimental Chemistry, Inorganic. Completely Illustrated with Full-page Engravings of all the Apparatus and Chemicals used in Experiments. For Students in High Schools and Junior Classes in Colleges, and Private Learners. By W. F. WATSON. New York: A. S. Barnes and Co. London: Gay and Bird, 22, Bedford Street, Strand. 1901. Pp. xviii.—320. Illustrated.

This volume has a pleasant appearance, and a closer examination shows it to be excellently adapted to the purposes for which it has been written. As stated in the preface, this text-book aims "to present the fundamental principles of elementary chemistry in a brief, clear, and logical manner, illustrating all important points as far as consistent by appropriate experiments."

The author recognises the fact that there are two classes of students who take an elementary course in chemistry, those intending to pursue the science by more extended studies, and those who complete their study in a single course; the latter is by far the larger class, and for them this book is admirable in many respects.

The subject is treated in a straightforward, common-sense way, with no peculiar fads incorporated, and the work is written in good strong English. easily compre-

hended by beginners, and avoiding childish expressions (supposed to be more easily understood) that will have to be dropped as the student advances.

The text is interspersed with no less than two hundred experiments, the directions for making which are clearly given without waste of words.

One peculiar, and as the reviewer thinks unwise, arrangement of matter must be noted; the important subject of *combustion* is first reached in Chapter XXXIV., after an elementary chapter on "Organic Compounds," and 88 pages further on in the book than the chapter on the "Atmosphere." Yet the two hundred and sixty pages preceding treat of phenomena and operations in which oxidation frequently plays an important part; it seems to the reviewer that Chapter XXXIV. might better follow Chapter XXIV.

As set forth on the title-page, one of the features of the book is the method of illustration. Twenty full-page reproductions of well-made photographs exhibit every piece of apparatus and every substance used in the experiments. These plates are artistically excellent, but fail in an important respect (easily remedied in a second edition) to accomplish their object. They are not accompanied by explanatory notes, and there is no reference to the individual apparatus in the text. Plate IV., for example, exhibits no less than six large apparatuses interspersed with sixteen or more bottles, dishes, &c., and the beginner finds no means to identify the special apparatus for generating hydrogen sulphide, or to distinguish it from the Woulfe apparatus for generating hydrogen chloride. If each figure on the plate bore a letter or number, and each plate was accompanied by a key, the use of the apparatuses might be clearly indicated. One extra page following each plate could be introduced in a second edition.

The Appendix contains a useful list of "Common Chemical Synonyms and Colloquial Terms," with their scientific equivalents; and many valuable tables of contents compactly printed.

Teachers of elementary classes will do well to give this book a thorough trial. H. C. B.

Researches on Cellulose, 1895—1900. By C. F. CROSS and E. J. BEVAN. London, New York, and Bombay: Longmans, Green, and Co. 1901. Pp. 180.

THERE is a good deal of confusion attaching to the use of the word "cellulose"; this is due to various causes, one of which is the curious specialisation of the term in Germany as the limited equivalent of "wood-cellulose." Another influence which the authors consider prevents the recognition of the obvious classification of the "celluloses" is the empiricism of the methods of agricultural chemistry. Physiologists, again, have their own views and methods in dealing with cellulose, and have had hitherto but little regard to the work of the chemist in differentiating and classifying the celluloses on a systematic basis.

After the Introduction, which deals with the general outline of the subject, and the criticisms which were written on the book entitled "Cellulose," published in 1895, the volume is divided into eight sections according to the table of contents, though in the letterpress there is little or nothing to indicate where one section ends and another begins; however, these sections comprise the general chemistry of the typical cotton cellulose, with a table giving the relative values of five methods of estimating the yield of "end-product" or cellulose; the final conclusion being that none of the processes fulfil the requirements of an ideal method. Schulze's method appears to give the nearest approximation to the "actual cellulose" of the raw material. Other sections deal with such matters as the decompositions of cellulose, such as throw light on the problem of its constitution; fufurroids, i.e., pentosanes and fufural-yielding constituents generally, the lignocelluloses, and the peptic group.

From the point of view of the chemist there has been a

very large development of the cellulose industries during the last five years, and this development is principally marked by the success of the newer ones; among these may be mentioned the treatment of the "roving" in the spinning frame, in flax-spinning, by the addition of reagents to the macerating liquid; the alkaline salts used are chiefly sulphite and phosphate of soda. There is a steady growth in the consumption of wood-pulps (cellulose). In regard to the paper trade of the world, this continues to be one of the most prominent characteristics of its evolution. There have been no important developments in the purely chemical processes involved in the several systems of preparing cellulose from wood. The acid methods (bisulphite processes) have developed much more extensively than the alkaline, the latter including the caustic soda and the mixed sulphide (Dahl) process.

The book is printed on Standard Printing Paper, made to the specification of the Society of Arts Committee (see page 160), and is supplied with two indices, one of subject-matter, the other of author's names.

Handbook on Petroleum for Inspectors under the Petroleum Acts. By Captain J. H. THOMSON and BOVERTON REDWOOD. London: Charles Griffin and Co. 1901. Pp. 298.

BESIDES being of practical utility to officers of local authorities under the Petroleum Acts this volume is intended, as indicated by its sub-title, "for those engaged in the storage, transport, distribution, and industrial use of petroleum and its products, and calcium carbide, with suggestions on the construction and use of mineral-oil lamps."

It is well known, the authors tell us, that only a small proportion of the petroleum used in this country is under direct control through the operation of the Petroleum Acts, but it is not a matter of equally common knowledge that arrangements, more or less adequate, are usually adopted to provide for the safe storage of such petroleum as is not under direct legal control.

In the present volume, which consists of eleven chapters and sixteen appendices, only such particulars of the geographical and geological occurrence of petroleum, and of its production and refining, are given as to afford an intelligent appreciation of the subject. The real object of the book is concerned with the safe storage, transport, &c., of petroleum.

One of the most important points in connection with the safe storage of petroleum is what is called "flash-point"; the broad principle on which such tests are carried out are as follows:—A sample of the oil to be tested is gradually heated up in a small vessel until, on the application of a light, a blue flame or flash is seen in the space above the surface of the liquid. The temperature of the oil is noted, and this temperature is commonly called the "flash-point" of the oil. This point, however, varies very considerably according to the conditions under which the tests are carried out, and to speak of the flash-point without giving the method by which it was arrived at is as meaningless as to mention a degree of temperature without saying whether Fahrenheit or Centigrade is meant.

Another method of testing petroleum consists in determining the temperature at which the oil takes fire and continues to burn when a light is applied to the surface; this is called the "fire test" of the oil, but though in use in several of the American States, it has never been adopted in this country except for lubricating oils. In Chapter VI. a large amount of information is given on this subject; in fact, we consider this chapter to be one of the most, if not the most, important in the book.

Chapters VII. and VIII. deal with the historical and legislative side of the question, while in Chapter IX. the precautions necessary with petroleum are fully given.

Chapter X. on petroleum oil-lamps is another important one, and contains much valuable information, both on the

choice of a lamp and their management. In this connection we think it as well to quote the following passage:—"It is not too much to say that 90 per cent of the accidents which have occurred, whether by explosion of a lamp or otherwise, have been directly due to gross carelessness, ignorance, or the use of lamps after they have become dirty or broken, or defective; these cases being aided by the mistaken economy which induces persons to buy cheap and flimsy lamps rather than those of safer and at the same time more durable construction."

The Appendices contain a good deal of miscellaneous information, though chiefly of a legislative kind; while the whole work cannot fail to be of great value to those for whose use it was written.

Coal-tar and Ammonia. By GEORGE LUNGE, Ph.D. Third and Enlarged Edition. London: Gurney and Jackson. Pp. 929.

THE growing importance and value of this work is well shown by its rapid increase in size since the first edition. That edition, which was published in 1882, consisted of 383 pages of letterpress and 88 diagrams; the second edition, published in 1887, contained 739 pages and 191 diagrams. This second edition having become exhausted, a third has been prepared consisting of 929 pages, and containing 285 diagrams.

The volume is divided into fifteen chapters, beginning with destructive distillation and the production and application of tar.

The production of coal-tar at the gas-works, tar and ammonia as by-products in coke-making, from gas producers and from blast-furnaces, and the properties of coal-tar and its constituents, are dealt with in Chapters II. and III. Chapter V. begins with some historical notes on the distillation of coal-tar; this was first carried out by Henry Hawkins in 1746, half a century before the first introduction of gas lighting, and a patent was granted to him on the 7th of August of that year; the principles of distillation appear quite clearly in this old patent. In succeeding chapters, VI. to X., the author goes fully into the production, properties, utilisation, &c., of pitch, anthracene oil, creosote oil, carbolic acid and naphthalene, light oil, and crude naphtha.

In Chapter XI. the rectification by steam is gone into, with a full description of ordinary and special steam-stills; the final products are also here fully described, and their applications discussed.

Chapters XII. to XV. deal entirely with ammonia, such as the sources from which it is obtained, the composition and analysis of ammoniacal liquor, and the properties of its constituents, the working up of ammoniacal liquors, and other technically important ammonium salts. This volume has been compiled with great care, and is thoroughly up to date; both the table of contents and the index are full and comprehensive.

Practical Organic Chemistry for Advanced Students. By JULIUS B. COHEN, Ph.D. London: Macmillan and Co. New York: The Macmillan Company. Pp. 284.

THE present volume is an enlargement of the one published in 1887, and has been completely re-written.

The chief additions are the introductory chapters on organic analysis and molecular weight determinations, and an extension of the appendix. Great skill is required in the manipulative part of organic chemistry, and success can only be achieved by constant practice and close attention to the rules and instructions given.

These instructions are set out with great clearness by the author, and will doubtless be of considerable value to the student.

The first forty-one pages briefly describe the methods of organic analysis; that is, the estimation of carbon, hydrogen, nitrogen, sulphur, and the halogens; also the determination of molecular weights by (1) the vapour-

density method, (2) the cryoscopic or freezing-point method, and (3) the boiling-point method. The remainder of the book is devoted principally to the preparation of the more familiar organic bodies; the materials required for the preparation are first given, then the method of procedure is minutely described; this is followed by equations and formulæ illustrating the reactions, and, finally, the properties of the body formed are given. The book is very clearly written, and well indexed.

Laboratory Companion for use with Shenstone's Inorganic Chemistry. By W. A. SHENSTONE, F.R.S. London: Edward Arnold. 1901. Pp. 117.

THIS book consists of a reprint of most of the experiments in Part I. of the author's "Inorganic Chemistry," together with a few other experiments and a number of exercises. It is intended merely as a laboratory companion, principally to save the larger work from being spoilt by the accidents which are inevitable with young beginners. The experiments are only qualitative, but are clearly though in many cases briefly described. If properly used the book will be of great assistance both to the teacher and his pupils.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

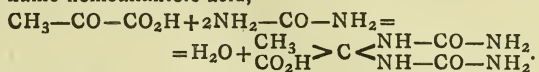
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 16, October 14, 1901.

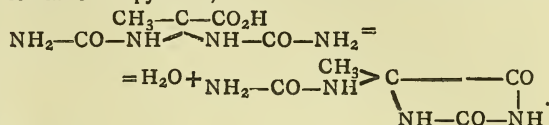
New Series of Experiments Relative to the Action of Hydrogen Peroxide on Silver Oxide.—M. Berthelot.—The investigation of the reaction of hydrogen peroxide on silver oxide having given rise to much discussion, the author undertakes a new series of experiments, which seem to remove all doubt as to the formation of particular silver peroxides. These experiments establish, by rigorous comparative measurements, that the peroxide of silver formed during the first stages of the reaction behaves with regard to dilute acids in a perfectly different manner from ordinary silver oxide, with which formerly it was confused. During the course of this investigation he obtains numerical values for all constants by means of the calorimeter and chromometer, such as:—Heats evolved, gaseous volumes, composition by weight of the products obtained, and time occupied in the transformations. All these were formerly taken separately, and are now verified for the fourth time, after twenty years. In fact, this time the author repeats all the operations in a continuous series of precise measurements, executed without interruption, in a special vessel and without the intervention of other manipulations or auxiliary agents. The results of the experiments are given in various tables.

The Inversion-points of Dilution.—Albert Colson.—The specific heat of a solution is not the mean of the specific heats of its constituents. From this fact, it results that the heat of solution and the heat of combination are variable up to a definite point, at which point certain heats of solution change in sign at a definite temperature. M. Berthelot established the point of inversion from the specific heats, and controlled these calculations by direct experiments made on solutions of sodium sulphate and potassium carbonate. The author now investigates saline solutions at temperatures near 100°. He verifies M. Berthelot's experiments, and also he establishes the existence of a temperature at which the heat of dilution of any solution whatsoever of a salt is zero, and at which no physical or chemical change takes place. His experiments are carried out on an aqueous solution of marine salt, and a curve is drawn and described to illustrate the changes.

Action of Urea on Pyruvic Acid. Homoallantoic Acid and Pyruvile.—L. J. Simon.—The action of pyruvic acid and urea takes place in two phases. In the first, an acid compound is formed, to which the author gives the name homoallantoic acid,—

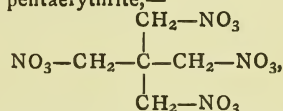


In the second phase, internal dehydration takes place between the carboxyl and one of the amine groups, with formation of pyruvile,—



By slightly modifying the conditions of the reaction, the author succeeds in isolating the intermediate body. It is highly probable that allantoic acid is obtained in the same manner, starting from glyoxylic acid. The reaction is similar to that already described for urethane. The action of water on homoallantoic acid is also examined.

Nitric Derivatives of Pentaerythrite.—Leo Vignon and F. Gerin.—The authors deduce from their experiments the following two conclusions:—1. That the nitrated derivatives of those alcohols having an open chain whose atomicity is equal to or greater than 4 manifest reducing properties with regard to cupro-potassic solution. For example, the tetranitrated derivative of erythrite, $(\text{NO}_3)_2\text{CH}_2\text{—CH}(\text{NO}_3)_2\text{—CH}(\text{NO}_3)_2\text{—CH}_2(\text{NO}_3)_2$, the nitrated derivatives of dulcitol (hexa), and of mannitol (penta and hexa) exhibit this reducing property, whilst the nitrated derivatives of methylic and ethylic alcohols, glycol, and glycerin do not. 2. That the tetranitrated derivatives of pentaerythrite,—



are void of all reducing power. It seems necessary, then, to admit that certain nitric ethers have a special constitution, and the authors intend to investigate this matter further.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., No. 11.

Contribution to the Study of Indium.—C. Chabrie and E. Rengade.—Already noticed.

A Molecular Combination formed by Iodide of Methyl and Methylic Alcohol.—J. Meunier.—While rectifying the product of the preparation of iodide of methyl by means of methylic alcohol, iodine, and phosphorus, without having previously removed the excess of methylic alcohol by washing with water, the author obtained a liquid boiling at 37.3° under 747 m.m., and at 37.9° under 760 m.m. This liquid is colourless, and resembles iodide of methyl when freshly distilled, but when exposed to diffused light it rapidly becomes coloured, and after a few days it has a decidedly brown appearance. It does not even remain colourless in the dark. The remarkable constancy of its boiling-point, and the fact of its composition answering to a definite formula, is sufficient to cause us to regard it as a definite compound; it has also another characteristic which confirms this view, and that is its vapour-density. Experiments, and analyses made, lead the author to the formula $\text{CH}_3\text{I} + \frac{1}{2}\text{CH}_4\text{O}$. To decompose this body it is sufficient to treat it with water, which dissolves the methylic alcohol; the iodide of methyl left after washing and drying over chloride of lime boils at 43.1° under 761 m.m. There is therefore a difference of 5° between its boiling-point and that of the molecular compound.

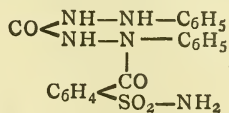
Action of different Alcohols on some Acetals of the Monovalent Alcohols.—Marcel Delépine.—Already noticed.

Glucamine: a New Base derived from Glucose.—L. Maquenne and E. Roux.—Already noticed.

Synthesis and Properties of the Nitrile-phenols.—Edmond Fiquet.—Take equimolecular weights of cyanacetic acid and one of the benzylic, *o*-*m*-*p*-toluic, cinnamic, &c., aldehydes. This mixture is placed in a flask with a long neck and the temperature raised to about the boiling-point of the aldehyde, then wait till the reaction commences; this takes place with the evolution of heat and steam. Withdraw the gas-burner, and allow the reaction to terminate spontaneously. The crystalline mass which forms on cooling is then purified by crystallisation in alcohol. To transform these bodies into nitriles with the normal chain, they are heated *in vacuo*. The body commences by melting, carbonic acid is then given off; when this ceases, the temperature is raised and the nitrile distilled. These phenols, when introduced into the organism, not only prevent the development of micro-organisms, but also neutralise the action of their products of secretion.

The Tetrachlorised Dimethyl and Diethylamidobenzoylbenzoic Acids and their Derivatives.—A. Haller and H. Umbgrove.—The examination of these acids shows that they occur under identical conditions under which the non-chlorised dialcylamidobenzoylbenzoic acids are prepared; that they differ from these latter, inasmuch that they cannot be etherified directly by the ordinary method, and they do not give dialcylanilinephthaleins when we attempt to condense them with the dialcylanilines by the help of acetic anhydride; that they form under these conditions tetrachlorised mixed acetyldialcylamidobenzoylbenzoic anhydrides, and that these anhydrides, treated with alcoholates of sodium, give rise to other salts.

Action of Saccharine on the Urea from Phenylhydrazine.—H. Défournel.—Saccharine does not combine with ordinary urea, but it does so with the urea from phenylhydrazine. A cold saturated solution is made of one molecule of saccharine in pure methylic alcohol. To this solution, one molecule of urea from phenylhydrazine is added. A certain quantity of this urea remains undissolved; it must therefore be heated to effect the solution. On cooling, a pale rose-coloured crystalline compound is formed; this must be re-crystallised from boiling methylic alcohol. The crystals melt at 98°; they are soluble in boiling water, and on the aqueous solution cooling the substance is precipitated. The results of their analysis shows that an organic saccharinate has been formed:—



The Basic Saccharinate of Quinine.—H. Défournel.—When we mix a solution of two molecules of saccharine in ethylic alcohol with a warm solution of one molecule of quinine we obtain, on evaporation to dryness, a syrupy uncrystallisable body, slightly soluble in cold water, fairly so in hot water, and easily soluble in alcohol, ether, and chloroform. This body is the neutral saccharinate of quinine. The basic saccharinate of quinine is obtained by evaporating on the water-bath a mixture of an alcoholic solution of one molecule of anhydrous quinine with an alcoholic solution of one molecule of saccharine; as in the former case, a syrupy non-crystallisable mass is obtained. The basic saccharinate of quinine can, however, be obtained in the crystalline form by following the general method for the preparation of the metallic saccharinates, which consists in effecting the double decomposition of saccharinate of soda and the metallic sulphates in aqueous alcohol, only, the metallic sulphate is replaced by sulphate of quinine.

MISCELLANEOUS.

The Ceric Sulphates.—W. Muthmann and L. Stützel.—The authors have repeated the analysis of these sulphates, about which such different opinions exist. The evaporation of a solution of ceric hydrate in dilute sulphuric acid always gave them a yellow salt in the form of fine needles; this was followed, but not always, by another reddish-brown salt in large crystals, this latter being decomposed by pure water. The yellow salt is ceric sulphate, $(\text{SO}_4)_2\text{Ce}+4\text{H}_2\text{O}$; the yellowish-brown salt is a ceroso-ceric sulphate, $(\text{SO}_4)_3\text{Ce}_2+2(\text{SO}_4)_2\text{Ce}+20\text{H}_2\text{O}$.—*Berichte*, vol. xxxiii., p. 1763.

The Quantitative Estimation of Ozone.—O. Brunck. In this paper the author describes the difficulties to be met with in the analysis of ozonised gases. By means of a series of experiments on the action of ozone on a neutral solution of iodide of potassium he arrives at the following practical conclusions:—1. The quantitative estimation of the proportion of ozone in a gas by means of a neutral solution of iodide of potassium leads to incorrect results, which are much too low. 2. Exact results can be obtained by using an acid solution of iodide of potassium. It is only when using a very concentrated solution that a small error is to be feared in consequence of the formation of hydriodic acid. This, however, can be allowed for by making a simultaneous blank experiment. 3. It does not matter whether sulphuric or acetic acid be used, but it is advisable always to use the calculated quantity of acid.—*Berichte*, vol. xxxiii., p. 1832—1842.

Wanted, Assistant for Research work, chiefly Organic, for a few months.—Apply by letter to H. Auden, Woodford Green, Essex.

Young Chemist (Organic), Ph.D., with knowledge of Physical Chemistry and Bacteriology, seeks employment with Analyst or in Works.—Address, Y. C., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

FOR SALE.—"Chemical Society Journals." Complete set (unbound), with Indices, 1875—1901. Best offers. Address, E., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

FOR SALE.—A very fine 1-25th Best Achromatic Objective, by Ross, of London. Cost £24, price £10. Can be seen at the Office of Mr. L. F. St. John, 33, Havelock Road, Hastings.

BOROUGH OF SOUTHWARK.

APPOINTMENT OF PUBLIC ANALYST.

The Council are desirous of receiving applications for the Appointment of PUBLIC ANALYST for the Borough from persons not exceeding 45 years of age.

The appointment will be subject to the approval of the Local Government Board.

Candidates must furnish proof of competent skill and knowledge of Analytical Chemistry, Therapeutics, and Microscopy, and must be holders of the diploma of Fellowship or Associateship of the Institute of Chemistry of Great Britain and Ireland, together with the Certificate granted by the Institute after an examination conducted by them in Therapeutics, Pharmacology, and Microscopy, and be competent to discharge the duties in accordance with the Sale of Food and Drugs Acts, 1875 to 1899.

The salary will commence at £400 per annum, rising by annual increments of £25 to a maximum of £500 per annum, the Council providing a laboratory, apparatus, and all necessary assistance at a cost not exceeding £300 per annum.

The person appointed will be required to devote the whole of his time to the service of the authority and discharge such duties as they may require. The appointment will be made on the understanding that there will be no pension or superannuation allowance.

Forms of application with particulars of the appointment may be obtained from the undersigned.

Applications on the prescribed form, accompanied by not more than three testimonials, and endorsed "Public Analyst," must be sent to me not later than 4 o'clock on Wednesday, the 20th day of November 1901.

Personal canvassing will disqualify.

J. A. JOHNSON,
Town Clerk.
Southwark Town Hall,
Walworth Road, S.E.,
November 6, 1901.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2190

ON THE PLACE OF HYDROGEN IN THE PERIODIC SYSTEM.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.

WITHIN recent times Mr. Masson's view that hydrogen is the first member of the halogen group has been preferred by such eminent chemists as Sir William Crookes and Professor Ramsay to the old view that it stands at the head of the first group in the periodic system.

Professor Ostwald in his recently edited "Grundlinien der Anorganischen Chemie," the most modern of all books on inorganic chemistry, in which, however, the periodic system is *not* taken as a basis of the treatment of elements, but only brought in an appendix, also places hydrogen at the head of the halogen group. It may be mentioned that Ostwald places the elements Cu, Ag, Au in two quite different groups, and that he has introduced a new group for "other elements," many of which might have very well been placed in natural groups corresponding to those of the periodic system.

It has been for some time my intention to express my opinion on this important question, and I am very glad that this question was treated quite recently by Mr. Geoffrey Martin (CHEM. NEWS, lxxxiv, pp. 154—155).

While agreeing with most of Mr. Martin's arguments I do not partake his view that "it is needless to give any other examples"; for such an important and by no means simple question ought to be treated as fully as possible in order to prove definitely that only the older view is correct, whereas the view recently proposed is quite untenable.

Before bringing our own arguments let us see first what is the opinion of the chemist who may be regarded as the real founder of the periodic system of elements, and, as I may say, of the modern part of chemistry connected with it. Undoubtedly, chemical elements had been arranged long before Mendeleeff in a manner approaching more or less our present form of the periodic system, but all these arrangements possessed not much more than the outer form, whereas Mendeleeff established his periodic law:—"The properties of elements and of the simple and compound bodies formed of them, as well as the combining forms of elements, are periodic functions of the atomic weights," and by saying, "it will be impossible in the future to consider chemical elements and their compounds without taking the periodic system (and the periodic law) as a point of departure," he opened up anew the old department of inorganic chemistry, the interest for which had nearly vanished in comparison with the astonishing development of modern organic chemistry, worked up upon the basis of the doctrine of valency and chemical structure.

Everyone knows what a great help the periodic system has proved in teaching and studying chemistry, and especially those who are survivors of the ante-Mendeleeffian period, are aware of the incomparably greater pleasure and satisfaction which is afforded by the experimental work in inorganic chemistry, since we are able to conduct it in the spirit indicated by Mendeleeff. Modern physical chemistry with its new methods and views has, of course, greatly contributed to the *renaissance* of inorganic chemistry, but it is not the place to dwell upon this question here.

1. Mendeleeff does not simply place hydrogen "at the head of the alkali metal group," as Mr. Martin does; on the contrary, he shows that there is a marked difference between hydrogen and the latter, for he speaks in his

well-known fundamental paper of the difference between the "typical elements" and the other elements of the same group; the former exhibiting, like the first members of the homologous series of organic compounds, some properties which are not found in the higher members, and *vice versa*. "From this follows the *isolated, independent position of hydrogen* with the lowest atomic weight." "According to the (combining) form of its salt-like oxide, H_2O , and the salts HX it must stand in the first group; the nearest analogue of H is Na, which also stands in an *odd* series of the first group. The more remote analogues of H are Cu, Ag, Au."

I cannot repeat all he says about the later elements. It must suffice to say that they occupy a double position, in the *first* group and in the *eighth* group; in the lowest combining forms they correspond to H and Na (first group). In spite of a similarity of the combining forms, HX and NaX , there exists between both a whole series of generally known differences, the differences between carbonic acid and the homologous glycolic acids being similar to it in many respects.

As regards the similarity of the physical properties of the compounds of H' and Na' , Cu' , Ag' , and Au' he shows that their monochlorides have a molecular volume, very nearly equal, varying only between 26 and 29, whereas the volumes of $LiCl$ and KCl , *not belonging to this sub-group*, are 21 and 37. The same holds good in the case of other compounds.

All this shows that hydrogen does not simply stand "at the head of the alkali metal group."

2. According to Mendeleeff there are two kinds of oxides which must be strictly distinguished from another, viz., (a) the oxides of the water type, and (b) the oxides of the hydrogen peroxide type.

Among both kinds are found oxides behaving as *peroxides*. They are distinguished from ordinary oxides by possessing one or more "active" oxygen atoms, and by liberating from hydriodic acid an amount of iodine equivalent to the "active" oxygen. The peroxides of the water type are called by Schönbein *ozonides* (e.g., CrO_3 , Pb_2O_4 , Tl_2O_3 , Ce_2O_4 , Pr_2O_4 , &c.), whereas those of the hydrogen peroxide type are called *antozonides* (e.g., Na_2O_2 , BaO_2 , TiO_3 , La_2O_5 , Th_2O_7 , UO_4 , &c.).

Now the composition of all oxides of the water type, including the *ozonic* peroxides, is the *measure of valency* of the elements contained in them in combination with oxygen, which later is here normally divalent, whereas from the *antozonic* peroxides no conclusions as to the valency of the respective elements can be made, some of their oxygen atoms being apparently monovalent.

Mendeleeff has shown that the quantity of oxygen combined with two atoms of an element in oxides of the water type, including several "ozonides," reaches maximally the number of the group of the periodic system, in which the respective element stands; such oxides being called "limit compounds" (e.g., Tl_2O_3 —III., Pb_2O_4 —IV., Cr_2O_6 —VI., Cl_2O_7 —VII., Os_2O_8 —VIII), whereas the antozonic peroxides may be regarded as a kind of "ultra-limit compounds."

It is a general rule that an element which forms an antozonic peroxide in no case forms another oxide or ozonide of the water type containing a higher number of oxygen atoms than the antozonic peroxide.

It must first be admitted that the circumstance that there is an *enormous, thorough difference in chemical character* between hydrogen and the halogens, between their ions and between H_2O and the oxides of the halogen group, like Cl_2O , between the compounds of hydrogen and those of the halogens with the metallic and non-metallic elements, constitutes a powerful argument against the position of hydrogen at the head of the halogen group. How can such a positive element as hydrogen stand at the head of such negative elements as the halogens? * The maximum

* The elements standing at the head of a sub-group are *always* more negative or less positive than the higher members of that sub-group.

valency of chlorine = 7 is reached in Cl_2O_7 , whereas the highest hydrogen oxide of the water type is water itself, in which hydrogen is undoubtedly monovalent. In hydrogen peroxide hydrogen has no higher valency than one, and so the composition of water, which is a limit compound of hydrogen, indicates that hydrogen is in *maximo* monovalent. Hydrogen, therefore, cannot belong to the chlorine group, the limit compounds of which correspond to the valency = 7.

The objection that fluorine also has no higher valency than one is met by pointing to the circumstance that we do not know any oxygen compound of fluorine, and are therefore unable to speak of its valency towards oxygen. But fluorine, as a "typical element," possesses properties lying between those of the other halogens and those of the "typical" oxygen, which latter in closest analogy to the monovalency of fluorine, is hardly ever more than divalent, though it stands at the head of the *hexad* group. And yet it is not improbable from the constitution of compounds like KF.HF and some double fluorides that fluorine sometimes possesses a higher valency than one, whereas in the case of hydrogen we have a *certainly* that its *maximum* valency is one.

I would like to meet with still another objection. The odd numbers of the first group of the periodic system form a series of *higher* oxides than water:— H_2O_2 , Na_2O_2 , Cu_2O_2 , Ag_2O_2 , Au_2O_2 .

Why should we not regard *all* these oxides as possessing the same constitution, and *all* the elements themselves as higher than monovalent?

The answer is this:—The peroxides of hydrogen and sodium are ultra-limit compounds of *monovalent* elements of the *first group*, whereas the ordinary, respectively, ozonic oxides of copper, silver, and gold are divalent compounds of the elements of the *eighth group*. The maximum valency of these elements is probably *three* in copper (Cu_2O_3 ?), *two* in silver, and *three* in gold.

The circumstance that the position of hydrogen in its old, original place in the periodic system must be defended by rather complicated arguments, like the above, does, however, by no means prove that the view defended is incorrect.

Bohemian University, Prague.
October 22, 1901.

THE FREEZING-POINT OF VEGETABLE SAPS AND JUICES.

By WALTER F. SUTHERST, Ph.D.

THE injurious effect of frost on garden produce is a fact well known to gardeners and farmers, and it is at this time of the year especially when the precautions to counteract it are resorted to.

A temperature more or less below freezing-point must occur before any injury can be done, and this temperature is known to vary considerably for different species of plants. The degree of cold to which some plants can be subjected without damage is often very much below the freezing-point of the sap, which may be explained by the fact that liquids can be cooled much below their freezing-points without solidifying provided they are kept perfectly still—a condition usually present on a calm frosty night,—and then it is also possible for the sap to freeze and thaw again without any damage to the structure whatever.

This property of resisting frost induced me to find the freezing-points of the sap or juice of some of the more common vegetables and fruits, and the results agree pretty well with one's experiences in this matter.

The method adopted for these determinations was as follows:—An average sample of the vegetable or fruit—about half-a-pound—was reduced to a fine pulp by means of a grater; the mass then strained through muslin and filtered through thick filter-paper. Five c.c. of the sap

were brought into a narrow test-tube containing a thermometer, and cooled down by a freezing-mixture of Glauber salts and concentrated hydrochloric acid. The results obtained were:—

	Freezing-point. °C.
1. Vegetable marrow—(a) Leaf and stalk ..	—0°75
(b) Fruit	—0°75
2. Swede turnip—(a) Leaf and stalk	—1
(b) Bulb	—1
3. Celery—(a) Green stalk and leaf	—1°4
(b) White portion	—0°75
4. Carrot—(a) Leaf and stalk	—1°2
(b) Root	—1°0
5. Cabbage—(a) Outside leaf	—1°1
(b) Heart	—0°85
6. Apple	—1°4
7. Pear	—1°75

It will be seen from the above figures that—(1) Those vegetables easily attacked by frost, *e.g.*, vegetable marrow, have the higher freezing-points; (2) the sap in the parts exposed to the air has the same freezing-point, *e.g.*, fruit and stalk of the turnip and marrow; while (3) those plants which have a portion in the ground, *e.g.*, celery and carrot, or protected, *e.g.*, cabbage heart, the sap in these portions freezes sooner than the exposed. It is very possible that these differences can be accounted for by the fact that the hardy exposed parts contain a more concentrated sap, since more evaporation goes on there; also, pear-juice, containing more dissolved uncrystallised matter, freezes lower than apple-juice.

The Agricultural College,
Holmes Chapel.

RESEARCH ON THE OXIDES OF CHLORINE.

By A. REYCHLER.

To facilitate the checking of calculations I will first give a few data as to the strength of my titrated solutions. The solution of thiosulphate of sodium is decinormal; 1 c.c. is equivalent to 0°00355 grm. of chlorine (or 0°008 grm. of bromine, or 0°012685 grm. of iodine), and corresponds to 0°00135 grm. of peroxide of chlorine. The solution of permanganate of potash is also decinormal; 1 c.c. is equal to 0°0008 grm. of oxygen, and corresponds to 0°0039 grm. of peroxide of sodium, or again to 0°0023 grm. of sodium (peroxidised).

1. Peroxide of Chlorine and Caustic Potash.

Preparation of a Solution of ClO_2 .—220 c.c. of water were poured into a well-covered crystallising dish, and on the surface of the water a crucible was floated, containing 12 grms. of potassic chlorate treated with a cooled mixture of 44 c.c. of sulphuric acid, and 10 or 11 c.c. of water. The cover was then put on, and the action allowed to proceed for two hours. The water takes a yellow colour owing to the absorption of the gas produced, and the solution becomes of such a strength that 10 c.c. is equal to from 40 to 55 c.c. of thiosulphate; that is to say, from 0°0540 to 0°0742 grm. of ClO_2 . Under the above mentioned conditions, and at a temperature of 20°, accidents are of very rare occurrence. It did happen, however, that on one occasion when I had taken particular care to pulverise the chlorate very finely, the ClO_2 came off very rapidly, and terminated in an explosion.

The reaction between the peroxide of chlorine and the caustic potash is far from being instantaneous. When we

* A little hydrochloric acid is added to a solution of iodide of potassium, and then 10 c.c. of the solution of peroxide of chlorine. It is then titrated with the thiosulphate.

mix equimolecular solutions of the two substances (we can even use a slight excess of potash) the yellow colouration of the chlorinised gas persists for a considerable time. The chlorometric value of the mixture, shown in c.c. of thiosulphate, diminishes at first fairly rapidly, but the retrogradation becomes slower and slower, and the real value is not actually obtained until after several hours.

The following are the figures obtained from an experiment:—

To 200 c.c. of a solution of peroxide of chlorine, which equalled 880 c.c. of thiosulphate, and, consequently, contained 1·1880 grms. of ClO_2 , I added 18·6 c.c. of a normal solution of caustic potash (that is, 1 c.c. more than the theoretical quantity).

The chlorometric value of the mixture varied in the following manner:—

Time elapsed.	10 c.c. were equal to— Thiosulphate. C.c.	The 218·6 c.c. were equal to— Thiosulphate. C.c.	Colour of the mixture.
1·5 mins.	21·7	474	Intense yellow.
9·5 "	17·9	391	—
17 "	17·3	378	—
30 "	16·7	365	—
1 hr.	16·2	354	—
5 "	15·8	345	Pale yellow.
23 "	15·7	343	Practically colourless.

Thus, as we should expect, according to the well-known equation, $2\text{ClO}_2 + 2\text{KOH} = \text{KClO}_2 + \text{KClO}_3 + \text{H}_2\text{O}$, the chlorometric value of the whole goes down to about four-tenths of the initial value of ClO_2 used in the experiment:— $880 \times 0·4 = 352$ ·*

The concordance between what was foreseen theoretically and what actually occurred, seems quite sufficient when we consider that peroxide of chlorine generally contains a trace of free chlorine, and that during the operation described it is also partially decomposed into its constituent elements. The principal reaction is thus more or less complicated by the secondary transformations, $\text{Cl}_2 + 2\text{KOH} = \text{KCl} + \text{KOC}l + \text{H}_2\text{O}$ and $2\text{ClO}_2 = \text{Cl}_2 + 2\text{O}_2$, of which the first tends to keep the original chlorometric value constant, while the second produces an excessive retrogradation.

Remarks.—1. When the amount of potash is exaggerated (by taking, for example, eight times the theoretical quantity), the yellow tint lasts for a much shorter time, and the final value is established much sooner. The resulting solution has the property of decolorising a solution of indigo-carmin (an indication of the presence of a hypochlorite), but it does not turn iodised paper blue, on account of the too great pre-dominance of KOH. By the addition of hydrochloric or sulphuric acid it turns yellow very markedly, but acetic acid only causes a very slight change of colour.

2. If, instead of caustic potash, we substitute bicarbonate of potassium the reaction is retarded enormously.

II. Peroxide of Chlorine and Peroxide of Sodium.

While the transformation we have just described takes place with characteristic slowness, that which we are now coming to is instantaneous.

When a yellow solution of ClO_2 is added to a colourless solution of Na_2O_2 the mixture remains yellow so long as the second reagent is present in insufficient quantity; and it is not difficult to find experimentally, to within a drop or two, the quantity of Na_2O_2 , which is exactly necessary to produce the decolouration. The operation can also be performed in the inverse sense, and the exact amount of ClO_2 determined, to cause the commencement of the yellow tint with a known quantity of sodic peroxide. These two operations can be carried out with the same precision as a titration.

The reaction is accompanied with the evolution of oxygen, and the resulting solution possesses the following properties:—It is faintly alkaline (that is, if it has not previously been made acid), it has no action either on indigo-carmin or on iodised starch paper. It becomes distinctly yellow on the addition of hydrochloric or sulphuric acid, and to a much less marked degree with acetic acid. When acidulated with a trace of the latter acid, it decolorises indigo, turns iodised paper blue, and with nitrate of lead gives the characteristic precipitate of plumbic chlorite, viz., crystalline flakes of a sulphur-yellow colour, very light, and with a very brilliant lustre.

To carry out the quantitative study of the reaction I made use of a special piece of apparatus, consisting of a graduated burette, connected by a flexible tube at the bottom to a movable reservoir; at the top of the burette there is a glass tap, connected by another flexible tube, to a bottle fitted with a cork pierced with two holes; a funnel with a tap passes through the other hole. Before commencing the experiment the burette is filled with water right up to the tap at the top, which must be then closed; the bottle contains a measured quantity of a solution of peroxide of sodium. The apparatus is then connected together, and a known volume of a solution of peroxide of chlorine is run into the funnel with the tap closed. The operation then consists of opening the tap at the top of the burette, and regulating the flow of ClO_2 from the funnel so that it is just sufficient to produce a yellow tint in the bottle. At the same time the gas generated is helped to escape by shaking the bottle, and equalising the water levels in the burette and the movable reservoir by gradually lowering the latter. When the volume of gas appears to be constant the upper tap can be closed, the bottle uncorked, and the contents analysed. Firstly, the chlorometric value of the solution is obtained, after being decolorised, if we like, with a drop of the solution of peroxide of sodium. Then the quantity of oxygen given off is measured by the difference found between the volume of the water displaced in the gasometric burette and the volume of the portion of the ClO_2 solution used. To effect this the volume of the unused portion of this solution is measured; that is the part left in the funnel.

The following figures were obtained by this method:—

Solution of Peroxide of Sodium.—Ten c.c. were equal to 47·95 c.c. of permanganate, and, consequently, contained 0·1870 grm. of Na_2O_2 . Amount of this solution used, 10·1 c.c., contained 0·18887 grm. of peroxide (0·0775 grm. of oxygen).

For a special reason, which I shall explain later on, I did not here pay any attention to the caustic soda due to the solution of peroxide.

Solution of Peroxide of Chlorine.—Ten c.c. were equal to 43·8 c.c. of thiosulphate, and contained 0·0593 grm. of ClO_2 .

The quantity of this solution used up was 55·55 c.c., equal to 243·3 c.c. of thiosulphate, or 0·32845 of ClO_2 .

In the operation described I caused 67·5 parts of ClO_2 to react on 38·8 parts of Na_2O_2 . The equation $2\text{ClO}_2 + \text{Na}_2\text{O}_2 = 2\text{NaClO}_2 + \text{O}_2$ gives practically the same proportion, viz., 67·5 to 39·*

Oxygen given off.—58·75 c.c. at a temperature of 16°, under 670 m.m., that is 0·0779 grm. This weight is equal to that of the oxygen in the peroxide of sodium.

Chlorometric Value of the resulting Solution.—Ten c.c. of this solution were equal to 28·7 c.c. of thiosulphate according to the two methods:—1. Ordinary direct titration. 2. Addition of an excess of hydrochloric acid and distillation of the chlorine to be estimated. 65·65 c.c. of the solution corresponded, therefore, to 188·4 c.c. of thiosulphate; and as the ClO_2 used was equal to 243·3 c.c. of the titrated liquor, the chlorometric value of the whole decreased to about eight-tenths of its original value. Everything thus happened according to the equation pro-

* 2ClO_2 is chlorometrically equal to 10Cl, while KClO_3 is only equal to 4Cl. I have made quite certain by direct experiment that the presence of KClO_3 only affects the titration very slightly.

* The figures given can be relied upon, as also can the calculation, which is too long to be reproduced here, that the ClO_2 used only contained a minimum quantity of free chlorine.

posed above, and the final solution contained an alkaline chlorite.

Remarks.—When we dissolved peroxide of sodium we always observe, even when using very cold water, a fairly considerable evolution of oxygen, and the solution continues to decompose slowly, as is shown by the persistent formation of bubbles of gas. This solution, therefore, contains not only the actual peroxide but also some caustic soda. I have always been of the opinion that the presence of this latter body has no great influence on the reaction of which we have just established the formula, and I base my opinion on the relative slowness of the reaction which might take place between the peroxide of chlorine and the alkaline base.

III. Halogen Elements and Peroxide of Sodium.

The action of chlorine, bromine, and iodine on an alkaline solution of peroxide of hydrogen has already been the subject of much research, as can be seen by referring to the "Handbuch der Anorganischen Chemie," by Dammer (vol. i., p. 435), and also Baumann's papers in the *Berichte*, 1891, iii., p. 789. This action is so similar to that of peroxide of chlorine that I was induced to confirm it by several experiments. The following are the results I obtained with iodine by making this element react on a calculated quantity of the other reagent.

Solution of Peroxide of Sodium. Alkalimetry.—100 c.c. were neutralised by 21.26 c.c. of normal acid, and consequently contained 0.4890 grm. of sodium.

Titration with Permanganate.—100 c.c. of the solution under experiment corresponded to 166 c.c. of permanganate, and contained 0.3818 grm. of peroxidised sodium. The rest of the metal—that is, 0.1072 grm.—was in the state of hydroxide.

Solution of Iodine (and Iodide of Potassium).—100 c.c. were equal to 209 c.c. of thiosulphate, and contained 2.6512 grms. of free iodine.

As we did not succeed in determining experimentally (as in II.) the proportion in which it was best to mix the reacting substances, I had recourse to the following calculation:—For 23 parts of sodium, 126.85 parts of iodine were necessary; 100 c.c. of the sodic solution (0.4890 grm. of the metal) thus corresponded to 101.7 c.c. of the iodine solution (2.6969 grms. of the halogen element).

The mixture causes an abundant disengagement of oxygen, and the resulting solution was of a reddish colour and had a faintly alkaline reaction. It did not require to be acidulated to decolorise indigo-carmin or turn iodised paper blue; it contained a certain quantity of hypiodite. This latter salt evidently resulted from the action of the iodine on the soda; and, as 100 c.c. of our solution of alkaline peroxide contained 0.1072 grm. of hydroxidised sodium, a quantity of iodine weighing 0.5912 grm. and equal to 45.6 c.c. of thiosulphate could be detected by titration. In fairly good concordance with this theory, I found that 201.7 c.c. of the final solution was equal to 49 c.c. of thiosulphate.

As to the evolution of oxygen, I measured it in a special experiment, similar to that described in Part II. With 100 c.c. of solution of sodic peroxide and 101.7 c.c. of iodine solution, I obtained, at 15° under 760 m.m., 202 c.c. of oxygen; that is, 0.269 grm. of the gas. The weight of oxygen contained in the peroxide used for the experiment was 0.266 grm.

The result of these operations shows that the action of iodine on a partially decomposed solution of peroxide of sodium should be formulated in the following manner:—

Principal reaction .. $\text{Na}_2\text{O}_2 + \text{I}_2 = 2\text{NaI} + \text{O}_2$

Secondary reaction .. $2\text{NaOH} + \text{I}_2 = \text{NaI} + \text{NaOI} + \text{H}_2\text{O}$

The colour of the solution seems, further, to indicate that a small quantity of iodine remains free, and that a corresponding quantity, therefore, of peroxide ought to react on the hypiodite, giving iodide, oxygen, and the free base.

Chlorine and bromine have been the subject of similar

experiments, but I need not go into details. Suffice it to say that the results obtained with alkaline solutions confirm the general character of the equation $\text{Na}_2\text{O}_2 + \text{E}_2 = 2\text{NaE} + \text{O}_2$, in which E represents chlorine, bromine, or iodine. By comparing this conclusion with that arrived at in Part II., we see that E not only represents a halogen element, but also the group ClO_2 of peroxide of chlorine.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 13.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 226).

PART I.—SEPARATION OF URANIUM (continued).

Separation of Uranium from the Alkali and the Alkaline Earth Metals.

If a solution containing uranium, alkalis, and alkaline earths is precipitated with ammonia, a portion of the alkalis and alkaline earths is carried down by the ammonium uranate (Fresenius's "Quantitative Chemical Analysis," Sixth Edition, p. 533), thus preventing a complete separation.

Hillebrand (*Amer. Journ. Sci.*, 1900, x., 136) found that it is possible to completely separate uranium from the alkalis and alkaline earths by several precipitations with ammonia. In order to verify this statement, solutions containing a measured amount of standard uranium nitrate solution, and sodium and potassium salts, were precipitated by means of a slight excess of ammonia, and the solutions brought to boiling. The precipitates were washed with a warm 2 per cent solution of ammonium chloride, after which they were dissolved from the filters with warm hydrochloric acid (sp. gr. 1.10), and caught in beakers. The precipitation of the uranium by ammonia, in the presence of ammonium chloride, and from hot solutions, was repeated twice, and it was found that after three precipitations the ammonium uranate was free from alkalis.

Magnesium may be separated from uranium by means of ammonium sulphide in the presence of ammonium chloride (*Zeit. Anal. Chem.*, 1865, iv., 384), and also by ammonia in the presence of an excess of ammonium chloride. The latter method is the one ordinarily used (Fremy's "Encyclopédie Chimique," 1884, p. 86). To the solution containing uranium and magnesium, add ammonium chloride, and boil. When the solution becomes clear, add a slight excess of ammonia to the hot solution, and continue boiling for a few minutes. Filter while hot, and wash the precipitate with hot water containing ammonium chloride. Dry, ignite, and weigh the uranium as oxide.

The separation of uranium from barium, strontium, and calcium is usually done by means of sulphuric acid in the presence of alcohol (Fremy's "Encyclopédie Chimique," 1884, p. 86). The metals should be in solution as chlorides, having present the smallest possible amount of free hydrochloric acid. To the moderately dilute solution, add sulphuric acid, then alcohol, which precipitates the barium, strontium, and calcium, in the form of sulphates. The uranium in the filtrate is precipitated with ammonia, and weighed as oxide.

The separation of uranium from barium, strontium, and calcium, may be brought about by precipitating the uranium with freshly prepared ammonium sulphide (free from carbon dioxide) (Fresenius's "Quantitative Chemical Analysis," p. 534).

In 1885, G. Albigoff studied the action of mercuric oxide on uranium solutions, and found a means of

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

separating uranium from the alkalis and alkaline earths (*Liebig's Ann. Chem.*, 1886, ccxxxiii., 147). He showed that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, can be successfully employed for separating uranium from calcium. The latter method is, however, preferable to the first. He states that a complete separation of uranium from calcium, strontium, magnesium, and the alkalis can be effected by the use of mercuric oxide; it does not, however, afford a separation of uranium from barium. The precipitation is made by adding a slight excess of freshly prepared mercuric oxide (in the form of an emulsion) to the boiling solution which contains ammonium chloride or nitrate. The boiling is continued for a few minutes longer, and then rapidly cooled by placing the vessel into cold water. Wash the precipitate by decantation with a cold dilute solution of ammonium chloride. It is placed along with the filter in a platinum crucible, cautiously heated at first, after which the temperature is gradually raised, and finally ignited over a blast-lamp. The residue consists of pure U_3O_8 . The separation of uranium from the alkali metals by this method does not give any undue trouble, but when calcium and strontium are present they are rather hard to rid from the uranium precipitate. This difficulty is overcome by boiling several times, during washing by decantation, with a solution of ammonium chloride, and each time rapidly cooling the solution before pouring off the supernatant liquid. The calcium and strontium in the filtrate are determined by the ordinary methods after the removal of the mercury by hydrogen sulphide.

Separation of Uranium from the Alkali and Alkaline Earth Metals by Electrolysis of Acetate Solution.

Uranium is a very difficult metal to separate from the alkalis and alkaline earths by gravimetric methods; but by electrolysis an acetate solution of these elements a perfect separation can be effected (*Amer. Chem. Journ.*, 1879, i., 329; *Journ. Amer. Chem. Soc.*, 1898, xx., 279). It can be readily separated from sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, and barium. This method was used by E. F. Smith for separating uranium from the alkalis, the alkaline earths, and the rare earths in the analysis of certain rare minerals.

A very peculiar property of uranium is that it is not deposited as metal on the cathode, but as the hydrated protosquioxide. Molybdenum is the only other metal known which, like uranium, is deposited as oxide on the cathode.

Experimental.

This research was made in order to fully confirm the reliability of the electrolytic method for the estimation of uranium and its separation from the alkalis, and also to find the conditions which are best suited for rather dilute solutions.

The cathodes for the first six experiments, when a current of $N.D_{140}=0.6$ to 0.7 ampère was employed, were two platinum dishes of about 250 c.c. capacity. For experiments Nos. 7 to 10, the cathode was a platinum dish of about 150 c.c. capacity.

The anodes were made of heavy platinum wire. One was made of 30 c.m. of No. 12 gauge platinum wire wound into a flat spiral of 4 c.m. diameter. The other anode was made of 37 c.m. of No. 14 gauge platinum wire wound into a flat spiral of 4 c.m. diameter. The results obtained by the use of either anode were the same.

Storage cells were the source of current.

For the electrolysis, a measured amount of standard uranium nitrate solution was run into a cleaned and weighed platinum dish. A known amount of sodium acetate and of acetic acid was added, and the solution diluted to a definite volume. After heating to about $60^\circ C$., the current was started, and the electrolysis continued till the solution was clear and colourless, and no uranium was indicated when about 2 c.c. of the electrolyte was removed and tested with potassium ferrocyanide in the presence of hydrochloric acid. As soon as all the

uranium was precipitated, the current was interrupted and the electrolyte was emptied into a beaker. The black deposit was several times washed with warm distilled water. The electrolyte and washings were then poured through a fluted filter, so as to prevent the loss of any particles of the deposit which are apt to be removed during washing. The filter was washed with warm water, dried over a Bunsen flame, ignited, and added to the dish. The dish was ignited at "redness" for about fifteen minutes, after which it was allowed to cool in a desiccator. The dish was weighed, and the final weight taken when it had remained on the balance pan for about five minutes, thus allowing its weight to become constant.

The deposit consisted principally of black hydrated protosquioxide of uranium ($U_3O_4 \cdot 3H_2O$), which on ignition changed to U_3O_8 .

At the beginning of the electrolysis the deposit formed as yellow uranic hydroxide, but as the deposition continued it changed to the black hydrated protosquioxide. The results obtained* are given in Table II.

These results were obtained by electrolysis a solution of 200 c.c. volume with a current of $N.D_{140}=0.55$ to 0.65 ampère.

The results obtained, when a solution of 125 c.c. was electrolysed with a current of $N.D=100=0.70$ to 1.50 ampère, are given in Table III.

According to the above results, the best conditions for the electrolytic precipitation of uranium from a rather dilute acetate solution are as follows:—To the solution containing about 0.10 gm. of U_3O_8 add from 1 to 2 grms. of sodium acetate (if alkalis are present, no sodium acetate is needed), and from 1 to 2 c.c. of 50 per cent acetic acid, or if glacial acetic acid is used only half the quantity is needed. Dilute to from 125 to 200 c.c., heat to about $65^\circ C$., and electrolyse with a current of $N.D_{140}=0.60$ to 0.70 ampère, and 6 to 8 volts. The uranium is completely precipitated in from five to seven hours.

With solutions containing about 0.15 gm. of U_3O_8 more current is necessary, and the best conditions are:—Add from 1 to 2 grms. of sodium acetate, and from 1 to 2 c.c. of 50 per cent acetic acid, dilute the solution to 125 c.c., and electrolyse with a current of $N.D_{100}$ = from 0.70 to 1.0 ampère. The temperature of the solution should be about 65° to $70^\circ C$. After the current is started no heat need be applied outwardly, as the current itself keeps the solution heated. The time required for the complete precipitation of about 0.15 gm. of U_3O_8 is from six and one-half to seven and one-half hours.

When solutions containing more than 0.15 gm. of U_3O_8 were electrolysed, some difficulty was experienced in precipitating all within eight hours by a current not exceeding $N.D_{100}=1$ ampère. With a current greater than this the deposits were very spongy, and peeled from the dish; so the amount of U_3O_8 in solution should not exceed 0.15 gm.

The electrolytic precipitation of uranium has been used a number of times for the estimation of uranium and for separating it from the alkalis and alkaline earths. The results obtained were concordant with those obtained by precipitating it gravimetrically.

The simplicity of the electrolytic method for the determination of uranium, and the short time required, are in favour of this method.

Separation of Uranium from Phosphoric Acid. Review of Methods.

Reynoso's Method (*Liebig's Ann. Chem.*, 1852, lxxxii., 368).—The uranium compound should be in solution as nitrate, having a small amount of free nitric acid present. Dilute to about 150 c.c., add a strip of pure metallic tin, and boil. The phosphoric acid unites directly with the tin, to form oxyphosphate of tin, which is insoluble. The

* This part of the work, including experiments 1–6, was done under the direction of Prof. E. F. Smith at the University of Pennsylvania, during April, 1900.

TABLE II.

Experiment No.	Grms. of sodium acetate.	Amount of glacial acetic acid.	Dilution.	Current.		Temperature.	Time, in hours.	Theoretical amount of U_2O_8 taken.	Weight of deposited U_2O_8 .
				Current N.D. ₁₄₀ = ampère.	Volts.				
1.	2	0.7 C.c.	200	0.55	5	68-70	8	0.1098	0.1095
2.	2	12 Drops.	200	0.60	5	70	7	0.1098	0.1097
3.	2	0.5 C.c.	200	0.60-0.65	8-6	68-75	5	0.1098	0.1100
4.	2	0.5	200	0.65	8-7.3	65-67	5½	0.1318	0.1319
5.	2	0.5	200	0.65	7.5-6	68-70	5	0.1318	0.1318
6.	2	0.5	200	0.60-0.65	8-5.5	69-71	5½	0.1318	0.1320

TABLE III.

Experiment No.	Grms. of sodium acetate.	Amount of 50 per cent acetic acid.	Dilution.	Current N.D. ₁₀₀ = ampère.	Temperature.	Time, in hours.	Theoretical amount of U_2O_8 taken.	Weight of deposited U_2O_8 .
7.	1.0	2 C.c.	125	0.70-0.85	80-85	6	0.1361	0.1363
8.	2.0	2	125	0.70-0.93	70-80	6½	0.1814	0.1816
9.	2.0	2	125	0.95-1.50	70-75	7½	0.2268	0.2270
10.	0.3	1	125	0.90-1.30	73-80	8	0.2268	0.2260

precipitate is filtered off and thoroughly washed. The filtrate is made alkaline with ammonia, and the precipitate which forms is treated with acetic acid. If it does not entirely dissolve, nitric acid is added and the precipitation by pure metallic tin repeated (Fremy's "Encyclopédie Chimique," 1884, p. 86). Heat the solution to boiling, filter off the oxyphosphate of tin, and wash with warm water. The precipitate rarely contains any uranium. The tin in the filtrate is removed by means of hydrogen sulphide. The filtrate from the tin sulphide is boiled till all hydrogen sulphide is expelled, after which the uranium is determined by any of the ordinary methods.

W. Hintz (*Liebig's Ann. Chem.*, 1869, cli., 216) had occasion to investigate this method, and stated that a complete separation of phosphoric acid from uranium is effected by means of metallic tin.

Knopp and Arendt Method (*Chem. Centrbl.*, 1856, 773).—The separation of uranium from phosphoric acid may be effected by fusing the ignited mass of uranium and phosphoric acid with a mixture of potassium cyanide and potassium carbonate, and treating the fused mass with warm water to dissolve out the phosphoric acid as soluble alkaline phosphate. The uranium is left as protoxide, which is re-ignited and weighed, or else dissolved in acid and precipitated by ammonia. The phosphoric acid in the filtrate is precipitated with magnesia mixture and weighed as magnesium pyrophosphate. Hintz (*Liebig's Ann. Chem.*, 1869, cli., 216) used sodium carbonate in place of potassium carbonate, and obtained very satisfactory results.

E. Reichardt's Method (*Zeit. Anal. Chem.*, 1869, viii., 116; *Bull. Soc. Chem.*, 1873, xx., 347) is based on the direct precipitation of phosphoric acid from an acetate solution as uranyl-ammonium phosphate, provided the uranium is in excess. The precipitate is filtered off, washed, dissolved in a solution of sodium carbonate, and the solution added to a solution of magnesia mixture, which precipitates the phosphoric acid as magnesium ammonium phosphate. If iron is present it is first precipitated from a nitric acid solution by adding an excess of sodium carbonate and boiling (*Zeit. Anal. Chem.*, 1869, viii., 116). The phosphoric acid in the filtrate is precipitated as magnesium ammonium phosphate, and the uranium determined by the ordinary method, after expelling all the carbon dioxide.

Fresenius and Hintz Method (*Zeit. für Analytische Chemie*, vol. xxiv., p. 437; *CHEMICAL NEWS*, 1895, vol. lxxii., p. 206).—This method provides a means of separating arsenic and phosphoric acid from copper,

uranium, and iron. Have the solution feebly acid with hydrochloric acid, add an excess of potassium ferrocyanide, then saturate with sodium chloride. The ferrocyanide of copper, uranium, and iron are washed by decantations and subsequently decomposed by a warm solution of caustic potash, changing them to hydroxides. Filter and wash with a dilute solution of ammonium chloride till no ferrocyanide is recognised in the washings. The mixed hydroxides are treated with dilute hydrochloric acid. If any residue remains it is decomposed by a warm solution of caustic potash, going through with the same treatment as before. The solution by hydrochloric acid is free from arsenic and phosphoric acid. The copper, iron, and uranium are separated by ordinary methods.

Friedel and Cumenge (*Am. J. Sci.*, 1900, x., 135) separated phosphoric acid from uranium by dissolving the substance in nitric acid, and precipitating the phosphoric acid with ammonium molybdate.

This method was used (at the University of Pennsylvania in 1900) for estimating the amount of phosphoric acid in precipitates of uranous phosphate, which were formed by electrolysis. The sample was dissolved in 30 c.c. nitric acid (sp. gr. 1.42) and 3 c.c. hydrochloric acid (sp. gr. 1.20). When iron was present, the sample was dissolved in a mixture of 20 c.c. hydrochloric acid (sp. gr. 1.20) and 10 c.c. citric acid (sp. gr. 1.42). The solution was diluted to about 100 c.c., and nearly neutralised with ammonia. A few drops of nitric acid were added to clear the solution, making it slightly acid, then to the hot solution (not above 65° C.) 50 c.c. of molybdate solution* for every decigram. of phosphorus pentoxide present. After digesting at 65° C. for an hour and a half, the yellow precipitate was filtered, and washed with cold water. The filtrate was tested for phosphoric acid by adding more molybdate solution and re-heating at 65° C. The yellow precipitate of ammonium phosphomolybdate was dissolved from the filter with ammonia and hot water, and washed into a beaker to a bulk not exceeding 100 c.c. It was nearly neutralised with hydrochloric acid, cooled, and magnesia mixture added, drop by drop from a burette, stirring all the while. After about twenty minutes, 30 c.c. ammonia (sp. gr. 0.96) were added and the solution allowed to stand in the cold for three hours. The precipitate of magnesium ammonium phosphate was filtered and washed with dilute ammonia (2.5 c.c. ammonia and 100 c.c. water) till free from chlorides. The precipitate was dried, ignited, and weighed as magnesium pyrophosphate.

* Prepared according to the formulæ given in the "Official Methods of the U.S. Agricultural Chemists."

The uranium in the filtrate, from the ammonium phosphomolybdate, was determined by three precipitations with ammonia, and weighed as U_3O_8 .

(To be continued).

AMMONIUM PERSULPHATE AS A SUBSTITUTE FOR LEAD PEROXIDE IN THE COLORIMETRIC ESTIMATION OF MANGANESE.*

By HARRY E. WALTERS.

ALMOST everybody who has used lead peroxide in the colorimetric estimation of manganese has wished for a substitute which would dissolve completely in the acid solution, thereby allowing the comparisons to be made as soon as the solutions are cool. In the former method, it is necessary to use a centrifugal machine or allow considerable time for the finely-divided lead to settle. The substitute should be as cheap (or nearly so), act as rapidly, and be fully as accurate.

The writer has made a few experiments in the past with different substances, but without success, until, acting on a suggestion of Mr. Hugh Marshall's, which appeared in the *CHEMICAL NEWS*, vol. lxxiii., p. 76, that ammonium persulphate could probably be used for the quantitative estimation of manganese colorimetrically. Some of the salt was obtained and experiments instigated to find the proper procedure.

In all attempts to use the salt in solution in conjunction with the nitrate of silver (which is essential), the results were not satisfactory, owing to the slow decomposition of the persulphate, or the precipitation of the silver as peroxide, but where the salt was used direct with the requisite amount of nitrate of silver, very satisfactory results were obtained.

As the presence of a silver salt is essential for the oxidation of the manganese to permanganic acid, experiments were made to find the amount which should be present, and finally it was found that where 0.02 gm. of nitrate of silver was present the oxidation was complete. If much less than this be used, the oxidation will not take place, and, if too much be present, silver peroxide will separate and give an off-coloured solution difficult or impossible to compare.

Finally, the following scheme was adopted:—0.2 gm. of the test steel, and a standard steel of known manganese contents, are weighed off into suitable test-tubes; 10 c.c. of nitric acid of 1.20 sp. gr. are added to each. The tubes are placed in a water-bath and heated until dissolved, and all nitrous fumes are driven off. Fifteen c.c. of a solution of nitrate of silver, equal to 0.02 gm. $AgNO_3$ (1.33 grms. of the salt to 1 litre of water), are added to the tubes in the bath. This will cool the solution considerably. Now add immediately about 1 gm. ammonium persulphate salt to each, and continue warming until the oxidation commences, and then for about a half minute longer. Remove the tubes from the baths while the evolution of oxygen continues, and place in a cold water-bath. When solutions are cool, which will require but a few minutes, they are compared as usual. In case the manganese is high in the sample, 0.75 per cent and upwards, 0.1 gm. of the sample is taken.

The procedure for pig-irons and blast-furnace cinders is the same as for steel until the sample is dissolved, except that the cinders should be moistened before the addition of the acid; when in solution they should be filtered, in order to free them from the suspended matter. The paper is then washed, using the 15 c.c. of nitrate of silver solution

as the wash, and the procedure continued the same as for steels. If this filtration is not made, the suspended matter (the carbon or silica), which in the old method is mechanically separated by the lead peroxide, would give an off-colour to the solution.

In dissolving shot or chilled iron samples, it has been found good practice to add a little persulphate to the acid solution. This will destroy the combined carbon and aid the solution of the sample.

The following comparative results by the lead peroxide and ammonium persulphate methods show how well the results agree:—

	Lead peroxide. Per cent.	Ammonium persulphate. Per cent.
<i>Steels.</i>		
1.	0.33	0.33
2.	0.38	0.39
3.	0.40	0.39
4.	0.47	0.46
5.	0.58	0.58
6.	0.67	0.67
7.	0.75	0.75
8.	0.80	0.80
<i>Pig-irons.</i>		
1.	0.32	0.30
2.	0.65	0.65
3.	0.65	0.65
4.	0.70	0.69
5.	0.71	0.70
6.	0.77	0.75
7.	0.98	0.98
8.	1.02	1.02
<i>Cinders.</i>		
1.	0.23	0.24
2.	0.30	0.32
3.	0.32	0.32
4.	0.35	0.36
5.	0.40	0.40
6.	0.49	0.50
7.	0.70	0.72
8.	0.72	0.75

In making up the nitrate of silver solution it is preferable to make a stock solution by dissolving 33.25 grms. of the salt in a half litre of water. Ten c.c. of this diluted to a half litre will give the solution as used.

During the course of the experiments one interesting peculiarity of the salt was observed. While this peculiarity may be confined to this particular lot of the salt in question, it may be worth while to mention it to save others from the aggravation it caused us, and that is that when the salt is damp the reaction is very sharp and quick, but, when dry, it is very incomplete and irregular and not to be depended upon.

Ten one-pound bottles of the salt was the original order, and as soon as it was received the experiments were immediately commenced, correct results being obtained from this bottle and the following one. The balance had been stored in a rather warm place, and on opening the third bottle for use, trouble immediately commenced. After exhausting all seemingly possible and impossible causes, it was finally remembered that the salt in the previous bottles was damp, and 10 c.c. of water were added to the bottle, and intimately mixed with the salt. The trouble immediately disappeared. On drying some of the same salt it reappeared, so that now, a day or so before use, 10 c.c. of water are added to each one-pound bottle of the dry salt.

The advantages claimed for the ammonium persulphate method are:—

1st.—All the solution is obtained, there being nothing from which to decant, and the tube can be rinsed into the comparing tube.

* A Paper read before the Chemical Section of the Engineers' Society of Western Pennsylvania, September 19th, 1901. From the *Proceedings of the Engineers' Society of Western Pennsylvania*, xvii., No. 7.

2nd.—Only one-third as much acid is used as for the lead peroxide method.

3rd.—The small size of the test-tube that may be used—a one inch by eight inch tube replacing a one inch by ten inch tube, previously used, at only one-half the cost.

4th.—As the oxidation takes place below the boiling point of water, a simple water-bath can be used for the entire operation, thereby doing away with the heating over an argand burner, or hot plate, or the use of a calcium chloride bath, with the result that the breakage due to these higher temperatures is considerably reduced.

5th.—It is neater, quicker, and fully as accurate.

The use of the silver salt does not create much expense, as one grm. will make fifty determinations. The present price of the ammonium persulphate is \$1.00 per pound; in ten pound lots or more, 85 cents per pound. If the use of this method should become extensive, thereby creating a demand for the salt, it is reasonable to suppose that these prices would be greatly reduced. The comparative cost per hundred determinations, using the quotations of a local supply house, would be:—

Ammonium persulphate method ..	33.8 cents
Lead peroxide method	50.8 "

Using the quotations obtained by one of the mill laboratories the cost would be:—

Ammonium persulphate method ..	20.9 cents
Lead peroxide method	38.3 "

In conclusion, I would say that the method has been in use for some time at the laboratory of the Duquesne Steel Works and Blast Furnaces, and has given perfect satisfaction for all ranges of manganese.

The persulphate is also an excellent substitute for bromide in the oxidation of manganese in alkaline solutions. It has been found good practice to add the salt direct to the boiling solutions.

I also wish to acknowledge my thanks to Mr. J. M. Camp, chief chemist at the Duquesne laboratory, for many valuable suggestions in the writing of this paper.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1901.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

A PAPER on "A Voltammeter for Small Currents" was read by Dr. R. A. LEHFELDT.

The instrument consists of a capillary tube about 25 c.m. long, completely filled with mercury, with the exception of a bubble of mercurous nitrate solution, about 1 c.m. long, placed near the middle of the tube. Connection with the two mercury columns is made by means of platinum wires passing through the side of the tube. To use the instrument it is placed in a vertical position, the anode being at the top, and the quantity of electricity which passes through is measured by the change in volume of either electrode. In a test experiment the change in volume was measured by means of a micrometer, and agreed within 0.6 per cent with the amount deduced from the known value of the current. It is necessary that the currents should be small so as to avoid complications due to polarisation.

The CHAIRMAN pointed out that the presence of air in the tube would render the readings inaccurate, and asked if it was necessary to apply any temperature correction.

Dr. LEHFELDT said that it was quite easy to seal the tube without admitting air, and the temperature correction was negligible.

A "Note on a Paper by Prof. Fleming and Mr. Ashton entitled 'On a Model which Imitates the Behaviour of Dielectrics,'" by Dr. J. BUCHANAN, was read by the Secretary.

The action of this model depends on the viscosity of a liquid, and the diagrams derived from it show by their form that the motion of the pencil which traced them approximated closely to what may be expressed by the term "motion of a viscous fluid by diffusion." In other words, the displacement curves obtained from the model, and their derived velocity curves, are of the same form as the graphs of certain solutions of Fourier's well-known equation $\frac{dv}{dt} = K \frac{d^2v}{dx^2}$. Lord Kelvin has shown that the

potential and the current at any point in the wire of a cable can be expressed by appropriate solutions of this equation, and in the same manner by the use of solutions of this equation the diffusion of electricity into or out of the dielectric of a condenser can be treated. It appears, therefore, that the motion of the model and the diffusion of electricity in a dielectric are subject to one and the same mathematical law. The author suggests that the inventors should obtain hysteresis diagrams by cyclical loading of the springs.

Prof. J. A. FLEMING said he was glad that Dr. Buchanan had drawn attention again to the model, because there were points about it which might be amplified with advantage. After giving a short description of the apparatus, he said that Dr. Buchanan had shown that mathematically the theory of the model was the same as that of diffusion in a cable, and he suggested that there might be something more than mathematical analogy. Prof. Fleming referred to the discussion on the original paper, in which Prof. Ayrton asked in what respect the model served its purpose better than a twisted wire. A twisted wire cannot represent the properties of a dielectric, because if twisted beyond the elastic limits there is a permanent set. There is no permanent set in the present model. He would like to know if a dielectric has a true conductivity, and suggested that experiments should be made by subjecting a dielectric to constant electric pressure at constant temperature, for years if necessary, and observing whether the curve of current becomes asymptotic to the zero line, or to a line parallel to it. The model could be made to represent a conduction as well as a displacement current by so arranging the bottom piston that it could descend but not return. The fact that the movements of the model were similar to the diffusion of current in a cable suggested that the process of conduction in a metal was similar to that of displacement in a dielectric.

Mr. J. MACFARLANE GRAY read a "Note on the Numerical Value of the 'Characteristic' of Water."

The author referred to a paper on thermodynamics which he wrote twenty years ago, and in which he supported the theory of a granular ether under enormous pressure. This theory easily explains the properties of bodies. There is a numerical characteristic for every substance in the state of vapour. This characteristic can be deduced from an analytical expression involving certain physical data which must be experimentally determined. His original number for water was 25.30693, but later experiments by Lord Rayleigh on the weight of hydrogen have altered this number to 25.33776. The author's original value for the absolute specific heat of water was 124960 "m.m. lift at Paris," but recent experiments of Callendar give 126230. According to the author's theory, water commences to freeze at 95° F., and the variation of the specific heat of water at low temperatures is due to the latent heat of ice. The formation of ice particles also explains the peculiar changes in volume of water as it cools to the freezing-point.

The CHAIRMAN asked if this theory could explain the fact that water can remain liquid below 32° F.

Mr. MACFARLANE GRAY said it could.

The Society then adjourned until November 22nd, 1901.

NOTICES OF BOOKS.

The Cost of Food; a Study in Dietaries. By ELLEN H. RICHARDS. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1901. 12mo. Pp. 161.

THE previous works by Mrs. Richards, "The Cost of Living as Modified by Sanitary Science," "Food Materials and their Adulterations," "Air, Water, and Food," together with the one under review, combine to establish her as an earnest student of the controlling factor in all life-food supply, and competent to give publicity to her theories as well as to make known the facts she so laboriously collects.

In successive chapters are discussed the kind, quality, and cost of food required and suited to infants, children at school, active youth, college students, brain workers, travelling and professional men, as well as persons in pauper and penal institutions, and hospitals. Subjects further dwelt upon are the general principles governing dietaries and lists of dietaries, with the exact cost per day per person. A very useful glossary of terms and a bibliography of the recent literature close the carefully prepared volume.

The author endeavours to show the relative cost of the right amount of the food-stuffs when derived from the various food materials. She recognises that this is largely influenced by the preparation and combination to which the food is subjected outside the body, as well as by the "mental and physical condition of the body receiving" it.

The author condemns the intemperance and wastefulness in food so very common in the United States, and uses the following language with regard to indulging children.—

"It is also true that a taste for highly spiced food, for sweets, &c., may be fixed by a very little unwise indulgence, especially since habit rather than instinct guides civilised man in the choice of food. It is the first taste that costs; no sane mother would give her child coffee or wine; why should she yield to its curiosity and give spiced foods and rich gravies? If the child is not taught to be whimsical and fickle in appetite, he will rarely make any remarks about his food. Alas, he usually hears too much for and against food, and as the parrot's vocabulary betrays his ship companions, so the child's fancies betray his parents and nurse."

The prices given for the various kinds of food are much cheaper than any with which the reviewer is acquainted; the author estimates, for example, the cost of coffee, milk, and sugar for six persons at one meal at twopence half-penny!

In an interesting chapter the author explains the process by which the dietaries have been computed. There is an index.

Recherches Rétrospectives sur l'Art de la Distillation. Historique de l'Alcool de l'Alambic et de l'Alcoométrie. By J. DUJARDIN. Paris: chez l'Auteur, 24, Rue Pavée. 1900. Pp. xvi.—236. 8vo. 125 Illustrations.

BESIDES the topics named in the title, this richly illustrated book treats of the history of wine, of the origin of alcohol, and of the knowledge of the alchemists concerning the operation of distilling, as well as the methods and apparatus used in later times. It is made up chiefly of extracts from unusual books and authors, arranged chronologically with a thread supplied by the compiler. Prominent are the works of Berthelot (with reference to the Greek and Arabian sources), Gesner, Brunswich, Agricola, Lemery, Barlet, Glauber, and others.

This method of compilation gives the book at first sight a disjointed look, but the reader must note that the author states in his preface that he has not prepared a scientific study, but simply a "pictorial and bibliographic history of alcohol and of the alembic." And as respects the repro-

ductions of engravings the book is eminently attractive, but the bibliographic part is insufficient; the data are not full, except in a few instances, the place of publication being generally omitted. The sources of the engravings are usually mentioned, but that of the very first plate (opposite page 2) is lacking. Again, the bibliographic data of a given book are not always given in the same order. (See Barlet, pages 91 and 116).

An interesting feature is the reproduction of entire pages of rare books, showing quaint typography and cuts. The author spent fifteen years collecting the material for this volume, and is to be congratulated on the result.

Unfortunately, there is no list of illustrations, and no index of subjects; merely an index of proper names.

The reviewer is tempted to transcribe the following short legend of Arabic origin which he recognises as a variant of the Talmudic version: "When Noah had planted a vineyard, Satan came and watered it with the blood of a peacock; when the leaves began to grow, he sprinkled it with the blood of a monkey; when the young fruit appeared, he used the blood of a lion; and when the bunches of grapes were quite ripe, he used the blood of a hog. The vines watered with the blood of these four animals acquired different characters. When the wine-drinker sips his first glass of wine, he becomes animated and vivacious, his colours become more gaudy, he acquires at this stage the brilliancy of a peacock; when the fumes of wine begin to affect his head, he becomes gay and he acts like a monkey; when thoroughly intoxicated with more drink, he becomes furious like a lion, and finally he lies down, stretches out to sleep, and behaves like a hog."

H. C. B.

Memorial Lectures delivered before the Chemical Society, 1893—1900. London: Gurney and Jackson. 1901.

THE thanks of all chemists are due to the Council of the Chemical Society for the publication of the valuable book now before us.

As is well known it has been the custom for some years past for the Chemical Society to commemorate deceased Foreign Chemists on its roll of Honorary and Foreign Members by a Memorial Lecture devoted to an account of their life and work. In every case care has been taken to select as the Lecturer some well-known chemist who by his intimacy with, and knowledge of, the special subjects to which the deceased *savant* had devoted his time, was peculiarly fitted to deal with such subject.

These lectures were originally published in the Society's Journal, but they will naturally be more available to the reading public in the form in which they now appear.

Besides giving an authoritative account of the genesis and development of most of the theories which lie at the root of modern Chemical Science, the lectures are in many cases themselves important contributions to science.

Without wishing to make invidious distinctions, we may mention the Helmholtz Lecture, by the late Prof. Fitzgerald; the Pasteur Lecture, by Prof. Frankland; and the Kekulé Lecture, by Prof. Japp, as being of special interest and importance.

With each lecture there is an excellent portrait of the chemist with which that lecture deals, and the whole forms a volume which should be found in every good library.

A Manual of Determinative Bacteriology. By FREDERICK D. CHESTER. London: Macmillan and Co., Limited. New York: The Macmillan Company. 1901. Pp. 401.

THE author undertook the important labour of arranging the several hundred bacteria which are known to science in such a manner that it would be more easy to identify any particular one, or at any rate, to determine whether it was already known or not. The amount of work involved in performing this task has been necessarily very

considerable, and the results are now embodied in the present volume.

The hope is expressed that by using this book as a laboratory manual the student will be able to identify a given culture, as is done with other organic bodies, without the expenditure of that great amount of labour which has made the identification of many microbes so serious a matter as to become almost impracticable.

The general scheme for the study of bacteria is given in Chapter II., on page 41, and is closely followed in Chapter III. by the classification of bacteria. In this chapter they are divided up, and arranged in various groups, according to their different properties, in a similar manner to the well-known analytical tables used for inorganic analysis, only in the present case the subject is a much more complicated one, and many more characteristics have to be sought after and confirmed, while the number of separate microbes is counted by hundreds. Following these tables, which occupy practically the whole book, we find a glossary of the terms used in descriptive bacteriology, a most useful adjunct to this comparatively new and complicated science.

The author has given us a valuable work which will be of great help to bacteriologists.

The Gas Engineer's Pocket-Book. Comprising Tables Notes, and Memoranda relating to the Manufacture, Distribution, and Use of Coal-gas, and the Construction of Gas Works. By HENRY O'CONNOR. Second Edition, Revised. London: Crosby Lockwood and Son. 1901. Pp. 454.

THAT this pocket-book has fulfilled its promise is shown by the necessity for a second edition. We have little to add to our remarks concerning the first edition, save that its usefulness is evidenced by its success. A few errors of the press have been corrected; the Statutory regulations for testing the illumination power and purity of gas have been added, and the text of the book amended where it was found advisable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 17, October 21, 1901.

The Limit of Chemical Reactions and that of the Product PV in Gases.—A. Ponsot.—The two hypotheses—"PV tends towards a limiting value when V becomes infinite," and "there are complete chemical reactions,"—are incompatible. However, the two hypotheses—"PV tends towards a limiting value for an infinite value of V," and "Chemical reactions are always limited,"—are compatible; also the two hypotheses—"P=0 for very large values for V," and "There are complete chemical reactions and also limited chemical reactions."

Action of Pyridic Bases on the Tetrahalogen Quinones. Hydroquinonic Derivatives.—Henri Imbert.—The author recently intimated that pyridic bases, of which the two α -positions are free, react on chloranile and bromanile, producing bodies having the constitution $R.C_5H_3N-C_6X_2O_2-OH$ or $\begin{matrix} R \\ | \\ OH \end{matrix} > C_5HN = C_6X_2O_2$.

These products, under the influence of bases, easily lose a halogen atom, which is replaced by OM' (M' being a monovalent metal). Acids set free a red body having the formula $R.C_5H_3N-C_6X(OH)O_2-OH$, assuming the pyridic formula, which is the most probable. In the pre-

sent research, the author assures himself that the quinonic function really persists in the molecule by reducing the body: $-C_5H_4N-C_6Cl_2O_2-(OH)$.

Oxidation of Benzenic Carbides by means of Manganese Dioxide and Sulphuric Acid.—H. Fournier.—The author examines the method of oxidation of various homologues of benzene by means of manganese dioxide and sulphuric acid. In the case of orthoxylene, he obtains a yield of *o*-toluic aldehyde of 37 per cent. Oxidation of pseudocumene by this method gives a yield of 22 per cent of aldehyde. In the case of paracymene, a very small quantity of aldehyde is produced.

Action of Ammonia on Benzyl Chloride, and Conditions of Formation of Benzylamine.—René D'hommée.—The reaction of ammonia on an halogenated ether usually gives a primary amine salt, with small quantities of secondary and tertiary salts of this alkali. Under certain circumstances, however, these latter predominate. The author examines the conditions which determine the course of these reactions, and he finds that in all his experiments benzylamine is chiefly produced in presence of a large excess of ammonia. The yield was as much as 44.5 per cent of benzyl chloride. To prepare the benzylamine in tolerably large quantity a yield of 42.6 per cent is best.

The Amine Derivative of the supposed Binaphthylene Glycol.—R. Fosse.—The amine which can be derived from the supposed binaphthylene glycol, and to which the formula $\begin{matrix} | & & | \\ C_{10}H_6-C-OH & & C_{10}H_6-C-NH_2 \end{matrix}$ has been attributed, is

in reality a derivative of dinaphthoxanthene, and possesses the formula $O < \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > CH-NH-CH < \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > O$. This is the bis-dinaphthoxanthene amine. Fuming hydric acids do not transform this amine into its salts, but decompose it into NH_4Cl or NH_4Br and mono-, chloro-, or bromo-dinaphthoxanthene, $X-CH < \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > O$. A solution of the amine in the hydric acids added to $PtCl_4$ gives the chloroplatinate of NH_4 and a double chloride of platinum and dinaphthoxanthene, $PtCl_4 + 2Cl-CH < \begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > O$.

Nitrated Derivatives of Arabite and Rhamnite. Constitution of certain Nitric Ethers.—Leo Vignon and F. Gérin.—The authors have already shown that nitric ethers of alcohols with an open chain, whose atomicity is equal or greater than 4, possess reducing properties with regard to cupro-potassic solution. These conclusions are now confirmed by a study of the nitrated derivatives of arabite and rhamnite, and also the authors examine the constitution of the nitric ethers of erythrite, mannite, dulcitol, arabite, and rhamnite.

Glycerophosphorous Acid and the Glycerophosphites.—Auguste Lumière, Louis Lumière, and F. Perrin.—Glycerophosphorous acid can be prepared by the action of phosphorus trichloride on glycerin, and from the acid a number of glycerophosphites are obtained. The greater number of these latter are soluble in water. A neutral solution of sodium or ammonium glycerophosphite gives no precipitate with salts of copper, iron, zinc, nickel, lead, mercury, or manganese; but with silver nitrate a white precipitate is obtained, which rapidly darkens. The calcium salt can be prepared in the form of a soluble powder, extremely soluble in water and deliquescent.

Journal de Pharmacie et de Chimie,
Series 6, Vol. xiii., No. 8.

Transformation of Creatine into Creatinine by a Soluble Dehydrating Ferment in the Organism.—Er. Gérard.—Already noticed.

Action of the Waters from Sétif on Lead.—Dr. Malméjac.—Numerous analyses have been made from time to time of the waters from Sétif, and these have been very concordant, giving the following results:—

Hardness	24°
Carbonic acid	13 c.c. per litre
Carbonate of lime ..	0.100 grm. "
Sulphate of lime .. .	0.052 " "
Sulphate of magnesia .	0.110 " "
Chlorides	traces

Total 0.262 " "

Three samples, of 100 grms. each, of this water were placed in glass vessels and left in free contact with the air. In the first, a strip of lead weighing 15 grms. was placed; in the second, a similar strip of lead fastened to an iron wire, which was also in the water; in the third, another similar strip of lead surrounded with copper filings. These were left for twenty days, when the following losses of weight were found to have taken place:—

No. 1.	0.02 grm.
" 2.	0.04 " "
" 3.	0.10 " "

After the first few days, in No. 3 tube a very voluminous precipitate was formed, which far exceeded that formed in either of the two other tubes.

Estimation of the Free Hydrochloric Acid in Gastric Juice.—Dr. Meunier.—In the quantitative estimation of free hydrochloric acid by colorimetric methods, two reagents in particular are used at the present time—that of Toppfer, with dimethylamidoazobenzol; and that of Gunzbourg, with phloroglucine vanilline. The first process is simple to carry out and rapid, but it is not very easy to read the exact change of colour. The other method, however, gives constant results when once sufficient skill has been acquired. The author now proposes a new method, which is a combination of these two, and gets very good results.

No. 9.

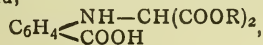
On Cinchonine.—E. Jungfleisch and E. Léger.—Already noticed.

Action of Caprylic Alcohol on its Soda Derivative. Synthesis of the Dicaprylic and Tricaprylic Alcohols.—Marcel Guerbet.—Already noticed.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mrs. Crowdy was elected a Member.

Formation of Indigo from the Malonic Ether of Anthranilic Acid.—D. Vorlander and C. Koettwitz.—The authors have observed that in the condensation of compounds containing the methine group, concentrated sulphuric acid, contrary to the alkaline methods of condensation, facilitates the elimination of water from the group in question. It is thus that the malonic ether of anthranilic acid,



and some other similar compounds are changed, when heated with concentrated sulphuric acid, into indigo-sulphonic acids. To prepare the diethylic ether from the tribasic acid, anthranilic acid is heated to gentle boiling for about three-quarters of an hour with the diethylic ether of mono-bromo-malonic acid and water; the ether formed melts at 127°. Its alcoholic solution is coloured a brownish-red by FeCl₃. The corresponding acid melts at 185°, and

behaves like the ether; with sulphuric acid it gives indigo-sulphonic acid, and by fusion with caustic potash it yields indoxyl or indigo. The neutral ether, fusible at 122–124°, obtained by reacting with bromo-anilonic ether on the ethylic ether of anthranilic acid, is not so easily transformed into indigo.—*Berichte*, vol. xxxiii., p. 2466.

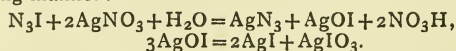
Action of Oxygen Gas on Cobalticyanide of Potassium, and on the Chromous Salts.—W. Manchot and J. Herzog.—It is known that a solution of cobalticyanide of potassium rapidly absorbs oxygen from the air; Zwenger (*Liebig's Ann. Chem.*, vol. lxi., p. 157) gives the reaction $8\text{KCy} + 2\text{CoCy}_2 + \text{H}_2\text{O} + \text{O} = 2\text{CoCy}_2\text{K}_3 + 2\text{KOH}$. The authors have observed that the volume of oxygen is about double that indicated by the preceding equation, and further, that notable quantities of peroxide of hydrogen are formed. They are of the opinion that this latter body results from the oxidation of the nascent hydrogen at first given off by the cobalticyanide; as a matter of fact, in the absence of air, solutions of CoCy_2K_4 , when warm and concentrated, give off free hydrogen. This has led them to compare the oxidation of the cobalticyanides with that of the chromous salts; with these latter the absorption of oxygen is much more rapid and the formation of peroxide of hydrogen is not observed; the same is the case with ferrous hydrate. The authors suggest the following experiment with chromous chloride:—A fragment of metallic chromium and some water are placed in a small flask fitted with a funnel furnished with a tap, and an escape tube; boil to drive out the air, then add hydrochloric acid; the chromium dissolves, giving off hydrogen plentifully; when the whole is dissolved, a blue solution remains. If we now continue to boil, small bubbles of hydrogen are given off and the solution becomes green.—*Berichte*, vol. xxxiii., p. 1742.

The Theory of Saponification.—J. Lewkowitsch.—It has been generally imagined that the triglycerides $\text{C}_3\text{H}_5(\text{OR})_3$ are entirely saponified according to the equation:— $\text{C}_3\text{H}_5(\text{OR})_3 + 3\text{MOH} = \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{MOR}$. There would, consequently, be no intermediate step characterised by the formation of a mono- or di-glyceride. This opinion has recently been challenged by M. Geitel, so the author has decided to settle the question in a definite manner. For this purpose he has made use of the degree of acetylation. This figure should always be nil if the saponification is complete, as the product freed by washings from glycerin and the soap formed would consist of a triglyceride and an acid ROH. It is true that we must not forget the action of acetic anhydride on this latter, an action which gives a small quantity of a mixed anhydride. Now the author has observed that the degree of acetylation is not nil, but that it varies considerably during the progress of saponification. (Naturally the degree of acetylation of the original material must be taken into account). Two other figures, viz., that of Hehner (insoluble acids), and the degree of saponification, were determined concurrently on samples taken after varying periods; these figures differ considerably from the limits corresponding to the acid ROH, and the triglyceride. The original paper gives a detailed description of the experiments carried out on tallow and cotton-seed oil. As saponifiers, lime and caustic soda were used.—*Berichte*, vol. xxxiii., p. 89.

The Double Metallic Thiocyanates.—A. Rosenheim and R. Cohn.—The following salts have been prepared by the mixing of solutions:—*Bromothiocyante of Mercury*, CNS.HgBr .—It forms beautiful needles, almost insoluble in water, soluble in warm alcohol. *Double Mercuric Thiocyanates*.—There are notably two well-crystallised salts of barium, one of which, $[(\text{CNS})_2\text{Hg}]_2\text{Ba}$, is slightly soluble, while the other, $(\text{CNS})_4\text{HgBa}$, is very soluble; the analogous double salts of NH_4 , K , Na , and Cu belong to one or the other of these types. *The Double Thiocyanates of Lead* are analogous to the preceding salts. *Double Thiocyanates of Cobalt*.—These occur as blue crystals, fairly soluble, giving solutions which are

blue when concentrated and rose-coloured when dilute:— $(\text{CNS})_4\text{K}_2\text{Co} + 4\text{H}_2\text{O}$, $(\text{CNS})_4\text{Na}_2\text{Co} + 8\text{H}_2\text{O}$, $(\text{CNS})_4(\text{NH}_4)_2\text{Co} + 4\text{H}_2\text{O}$, $(\text{CNS})_4\text{BaCo} + 8\text{H}_2\text{O}$. *Double Thiocyanates of Nickel*.—These occur as green crystals, very soluble in water, slightly soluble in alcohol, $(\text{CNS})_4\text{Na}_2\text{Ni} + 8\text{H}_2\text{O}$ and $(\text{CNS})_6\text{K}_4\text{Ni} + 8\text{H}_2\text{O}$. The *Double Thiocyanates of Aluminium or of Chromium* crystallise from a syrupy solution, $(\text{CNS})_6\text{K}_3\text{Al} + 4\text{H}_2\text{O}$ and $(\text{CNS})_6\text{K}_3\text{Cr} + 4\text{H}_2\text{O}$.—*Berichte*, vol. xxxiii., p. 1111.

Iodide of Nitrogen, N_3I .—A. Hantzsch.—Iodine reacts on nitride of silver, N_3Ag , giving rise to a new iodide of nitrogen, N_3I , which, in certain of its properties, resembles iodide of cyanogen. To prepare this body we shake up an aqueous emulsion of nitride of silver with a benzenic or ethereal solution of iodine (about one atom per molecule). The temperature must be kept down to 0° . We then decant the faintly yellow ethereal solution, dry over anhydrous sulphate of soda, and drive off the ether with a current of air, avoiding all traces of moisture and any elevation of temperature. The yellowish residue is washed with ligroin to remove the iodine, and more or less pure N_3I is left. This iodide is soluble in water, it has a piquant smell, and reacts on nitrate of silver in the following manner:—



The precipitate of iodide, iodate, and nitride is heated with dilute sulphuric acid, the hydronitric acid distilled over is titrated with decinormal nitrate of silver. The residue is treated with iodide of potassium, and the iodine set free is titrated with hyposulphite; this method has enabled us to ascertain the exact composition of the iodide of nitrogen. This iodide detonates even more easily than the iodides already known; it is soluble in most organic solvents, but the solutions formed gradually decompose with the evolution of nitrogen; the aqueous solution is neutral to litmus, and does not act on starch-paste. It decomposes according to the two following equations:— $2\text{N}_3\text{I} = 3\text{N}_2 + \text{I}_2$, $5\text{N}_3\text{I} + 3\text{H}_2\text{O} = 5\text{N}_3\text{H} + \text{HIO}_3 + 2\text{I}_2$. Alkalis act in the same manner.—*Berichte*, vol. xxxiii., p. 522.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 7.30. An Exhibition of "Some Antipoints seen under the 'Microscope,'" by Conrad Beck. "On Stereomicrography," by Prof. G. P. Girdwood.

Society of Arts, 8. Opening Address of the 148th Session, by Sir W. H. Preece, F.R.S., &c.

THURSDAY, 21st.—Chemical, 8. "On the Oxidation of Sulphurous Acid to Dithionic Acid by Metallic Oxides," by H. C. H. Carpenter. "Optically Active β -Hydroxybutyric Acids," by A. McKenzie. "On the Hydrochloride of Thiocarbamide," by H. P. Stevens. "The Constituents of the Essential Oil of Asarum Canadense," by F. B. Power and F. H. Lees. "Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide," by J. B. Cohen and H. D. Dakin.

FRIDAY, 22nd.—Physical, 5. "Multiple Transmission Fixed Arm Spectroscopes" and "On the Measurement of Young's Modulus," by Prof. W. Cassie. "Notes on Gas Thermometry—Part II.," by Dr. P. Chapuis.

Demy, 8vo, Pp. 584, Price 7s. 6d. net.

MEMORIAL LECTURES,

Delivered before the Chemical Society, 1893-1900.

With 14 Plates.

STAS, by Professor Mallet; KOPP, by Professor Thorpe; MARIGNAC, by Professor Cleve; HOFMANN, by Lord Playfair, Sir F. Abel, Bart, Dr. Perkin, and Professor Armstrong; HELMHOLTZ, by Professor Fitzgerald; LOTHAR MEYER, by Professor Bedson; PASTEUR, by Professor Frankland; KEKULE, by Professor Japp; VICTOR MEYER, by Professor Thorpe; BUNSEN, by Sir H. E. Roscoe; FRIEDEL, by Professor Crafts; NILSON, by Professor Pettersson.

London: GURNEY & JACKSON. 1901.

MACMILLAN & CO.'S BOOKS ON CHEMISTRY.

JUST PUBLISHED.

THE LABORATORY COMPANION TO FATS AND OILS INDUSTRIES.

By

Dr. J. LEWKOWITSCH, F.I.C., F.C.S.,
Consulting and Analytical Chemist and Chemical Engineer;
Examiner in Soap Manufacture and in Fats and Oils,
including Candle Manufacture, to the City
and Guilds of London Institute.

8vo, 6s. net.

Second Thoroughly Revised and Enlarged Edition.

CHEMICAL ANALYSIS OF OILS, FATS, WAXES, AND OF The Commercial Products Derived therefrom.

By

Dr. J. LEWKOWITSCH, F.I.C., F.C.S.

25s. net.

Second Edition, completely Revised and Enlarged.

MIXED METALS OR METALLIC ALLOYS.

By

ARTHUR H. HIORNS,
Head of Metallurgical Department, Birmingham Municipal School.

Globe 8vo, 6s.

Third Edition Now Ready.

BLOWPIPE ANALYSIS.

By J. LANDAUER.

Authorised English Edition by JAMES TAYLOR, B.Sc., Wh.Sc.,
A.R.S.M. Third Edition. Globe 8vo, 4s. 6d.

THE SCIENTIFIC FOUNDATIONS of ANALYTICAL CHEMISTRY Treated in an Elementary Manner.

By Professor WILHELM OSTWALD.
Translated by GEORGE M'GOWAN, Ph.D.

Second Edition. Crown 8vo, 6s. net.

SYSTEMATIC SURVEY of the ORGANIC COLOUR-
ING MATTERS. By Drs. G. SCHULTZ and P. JULIUS.
Translated and Edited, with extensive additions, by ARTHUR G.
GREEN, F.I.C., F.C.S. 21s. net.

THE GASES OF THE ATMOSPHERE. By Prof.
W. RAMSAY. 6s. net.

INTRODUCTION TO PHYSICAL CHEMISTRY. By
JAMES WALKER, D.Sc., Ph.D. Second Edition. 10s. net.

A COMPLETE TREATISE ON INORGANIC AND
ORGANIC CHEMISTRY. By Sir H. E. ROSCOE and Prof.
C. SCHORLEMMER. Illustrated. 8vo. Vols. I. and II. INORGANIC
CHEMISTRY. Vol. I. The Non-Metallic Elements. New Edition.
21s.—Vol. II. Metals. 31s. 6d.—Vol. III. ORGANIC CHEMISTRY;
The Chemistry of the Hydro-Carbons and their Derivatives,
Parts II., IV., and VI., 21s. Part III., 18s.

THE RISE AND DEVELOPMENT OF ORGANIC
CHEMISTRY. By C. SCHORLEMMER, LL.D. Revised Edition.
Edited by A. SMITHELLS, B.Sc. 5s. net.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By
Prof. IRA REMSEN. 8vo, 16s.

MANUAL OF PHYSICO-CHEMICAL MEASURE-
MENTS. By Prof. W. OSTWALD. Translated by JAMES
WALKER, D.Sc., Ph.D. Illustrated. 8vo, 7s. net.

MACMILLAN & CO., Ltd., LONDON.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2191.

THE PLACE OF THE RARE EARTH METALS AMONG THE ELEMENTS.

By B. D. STEELE, B.Sc. (Melbourne).

THE generally accepted classifications of the chemical elements, all of which are modifications of those first proposed by Mendeleeff and Lothar Meyer, are open to a common objection, in that they fail to assign any place to the metals of the rare earths. Many attempts have been made to assign to certain of these elements a position in one or other of the groups, and quite recently Brauner (*C. C.*, 1900, II., 524) has endeavoured to show that Prd may be placed in the fifth group and Nd in the sixth, since Prd forms an oxide, Prd_2O_5 , and he thinks that perfectly pure Nd would form an oxide, Nd_2O_6 (*C. C.*, 1898, I., 919).

such modification results in an increased power of generalisation and prediction.

In addition to the three elements predicted by Mendeleeff in 1869, and since discovered in Sc, Ga, and Ge, no less than fifteen new elements are indicated by the law in its present form as existing with atomic weights lying between those of Ce = 140 and Ta = 183, these being necessary to complete Mendeleeff's eighth, ninth, and tenth series. A considerable number of elements are known (the rare earth elements), which have these atomic weights assigned to them, but their properties are such that they require all to be placed in one, the third, group instead of being distributed through seven.

Julius Thomsen (*Zeit. fur Anorg. Chemie*, 1895, ix, p. 190) has suggested a classification whose essential features are the recognition of three chief groups of elements; the first containing two smaller groups of seven each, the second containing two groups of seventeen elements, and the third containing one, and probably two groups, of thirty-one elements each.

It has been generally taken for granted that if the gap between Ce and Ta were filled up we should have Mendeleeff's eighth and tenth even, and ninth uneven series completed.

Lothar Meyer supposed that his curve when completed would repeat in this section the periodicity so clearly

FIG. 1.

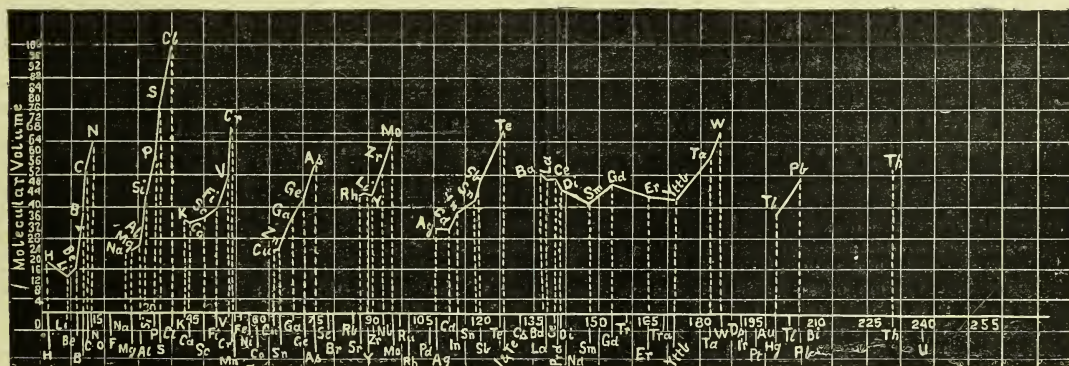
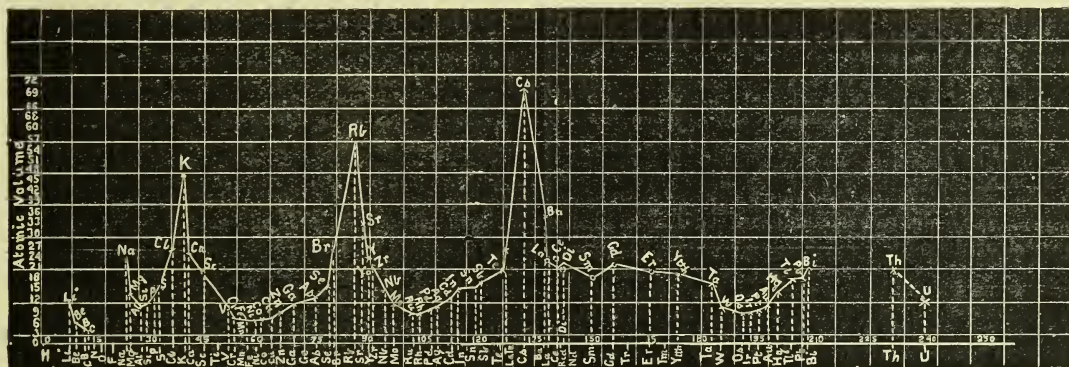


FIG. 2.

Such a mode of explaining the difficulty, however, does not seem to be consistent with a consideration of all the properties of the compounds of these elements.

Since the periodic law is an empirical law and is only an expression and classification of facts, by the aid of which it is possible to make predictions concerning the properties of discovered and the existence of undiscovered elements, we are justified in taking another and different course, that of modifying the form of the law, provided

shown in the other portions, and quite recently Stefan Meyer (*Monatsh. f. Chem.*, xx., 269), when comparing the atomic volume and the atomic magnetism, assumes the extension of the periodicity to this portion of the table.

It is a fact that no instance is known in which two elements of distinctly different properties occupy the same position in the periodic system, which would be the case if, for instance, ytterbium had assigned to it an atomic

weight $\frac{173}{3}$ or $173 \times \frac{2}{3}$; in the former case it would fall between Fe and Ni, in the latter between In and Sn. On the other hand, no elements other than the rare earth metals are known which occupy any position between Ce and Ta.

The question, however, arises as to whether the atomic weights usually given to these elements are the correct ones. That this is so is very probable, although this constant cannot be determined with as much certainty for these as for the other elements.

The recent investigations on "Magnetic Susceptibility," by Stefan Meyer (*loc. cit.*), and Du Bois and Liebknecht (*Ber.*, 1899, xxxii., 3344) have shown that in the series of the elements the atomic magnetic susceptibility of the element or the molecular magnetic susceptibility of the oxides reaches a maximum (paramagnetic) in two series of elements; the first being the series Cr—Co, the other being the group of rare earths.

In the series Ba, La, Ce, Prd, Nd, Sm, Gd, Er, Yb, Ta, the oxides pass from diamagnetism to paramagnetism between Ba and Ta, the paramagnetism rises rapidly through Ce, &c., to a maximum at Er, falling again through Yb, Ta being again diamagnetic, and throughout this series the susceptibility is much greater than anywhere else except in the iron group. From this and from a consideration of all the properties of these elements it seems that, whatever their atomic weights may be, they at least lie close together, and are arranged in their proper order. If therefore we can determine the atomic weight of one of these elements more certainty will be attached to those of the whole series.

From Nilson's (*Ber.*, xiii., 1433) determination of the specific heat of Yb_2O_3 it is possible to approximately calculate the atomic weight of Yb.

Assuming the atomic heat of oxygen to be 4, the atomic weight of Yb is thus found to be 164, which is sufficiently near the accepted number 173.

The only compound which exists for all the rare earths whose properties may be compared with the corresponding compound of the other elements is the oxide; and here the difficulty arises that we have to compare oxides of different types for different elements. Mendeleeff, however, has pointed out that if we consider the molecular volume of the typical salt forming oxides, a periodic variation is found to exist. No difficulty arises in the choice of oxide for the rare earths, since, in the majority of cases, only one is known to exist; exceptions being Ce, Prd, and Nd. For the two latter no data are available, and in what follows, therefore, the molecular volume of D_2O_3 is considered, and no radical difference is observed if D_2O_5 is taken for comparison instead.

By plotting the molecular volume of the oxide against the atomic weight of the element Curve I. is obtained, and it will be seen that the region of the curve under discussion is horizontal, and the periodicity so clearly shown in other parts is not reproduced.

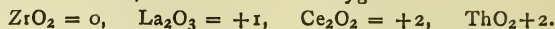
Unfortunately, data do not yet exist* for the completion of Lothar Meyer's curve of atomic volumes. Nevertheless, it is possible to calculate approximately the atomic volume from the molecular volume of the oxides.

The molecular volume of an oxide is not an additive property, since it is found that in the conversion of an element into its oxide very different volume changes take place according to the chemical properties of the element in question. Thus, for the strong alkalis and alkaline earths, the atomic volume of the oxygen in the oxide has a negative value, in acid oxides it has its greatest positive value; whilst for intermediate oxides and such as have only a slight tendency towards the formation of salts, the change in volume is least, and is nearly equal to zero.

This is clearly shown in the series of elements:—

	Na.	Mg.	Al.	Si.	P.	S.	Cl.	K.
A. V.	23.7	13.8	10.6	11.2	13.5	15.7	25.6	45.4
M. V. oxide	12	11.5	13	22.5	30	41	48	17
Vol. of O.	-22	-4.5	+1.4	+5.2	+6.2	+8.7	+6	-35

In addition, the volume of the oxygen is—



If therefore we assume for an approximation that the volume of the O in the rare earth oxides = 1.5, and then calculate the volumes of the elements, we may complete Lothar Meyer's curve. In this manner Curve II. is obtained, in which, as in Curve I., we see that the rare earths show no tendency to repeat the periodicity of the other portions.

The value for atomic volume has also been calculated for Sc, Y, La, Ce, Di, and the values so found show a very close agreement with the experimental figures.

As has already been mentioned, the figures for Di have been employed, as the density of Prd and Nd has not yet been determined.

Other properties of these compounds point also to the fact that the atomic volumes are not large. Thus, Stefan Meyer has shown that the elements with large atomic volumes are diamagnetic, whilst, on the other hand, the paramagnetic elements have small atomic volumes.

Similarly, Abegg and Bodländer (*Zeit. Anorg. Chemie*, 1899, xx., 453) have shown that the tendency towards the formation of ions is conditioned by the atomic volume; this tendency being much less with those elements which possess a small atomic volume.

From the preceding, the conclusion is drawn that the periodicity of the elements is such that there exist—First, two series of seven elements each. These are followed by a second two series of seventeen elements each, in each of which the first and the last seven repeat to a greater or less extent the properties of the first two series; the three intermediate elements in each long series forming an interperiodic group. Just as the periodicity of the first two series undergoes a change on passing to the third (long) series, so the fourth (long) series again undergoes a change in the form of periodicity on passing to the next series; the change being in this case again brought about by the introduction of what may be termed an interperiodic group—the group of the rare earth metals, which have several characteristics in common with the elements of the eighth (interperiodic) group. Thus the individual members are separated from one another only with the greatest difficulty, they occur together in nature, have very nearly the same atomic volume, and possess strongly marked paramagnetic properties.

The next series differs again from this in its periodicity. At present only two elements, Th and U, in this series are known to exist with absolute certainty; but, from the difference in atomic weight between Bi (the last known member of the preceding series) and U (which undoubtedly is correctly placed in the sixth group), it is evident that no series of elements will be found to exist in this position corresponding in place and properties to the rare earth elements.

The advantages that may be expected from a modification of the law in this direction are two:—Firstly, the clearing away of much confusion; and, secondly, an increased power of generalisation and anticipation. Thus, it is at once evident that the number of undiscovered elements is considerably reduced, the fifth and sixth groups being completed as far as Ta and Bi in the one case, and U and Te in the other. On the other hand, the fact that elements are lacking in the seventh group below Mn becomes more emphasised, as is also the case with the missing homologues of Te and I.

Moreover, should a further homologue of K be discovered, it will be found to have an atomic weight of about 218, and not 172. Such an element would occur in the same series with the well-known elements Th and U, in which are also probably the more doubtful elements

* Stefan Meyer (*Monatsh. für Chemie*, xx., 793) has determined the atomic volume of erbium, but says nothing about the purity or mode of preparation of the specimen of metal employed; it was obtained from Merck, and was probably very impure; it had a density 4.77, atomic volume = 34.9.

radium and polonium, which have been recently discovered. That radium has a very high atomic weight is shown by S. Curie (*Comptes Rendus*, 1900, cxxxi., 382; *CHEMICAL NEWS*, vol. lxxxi., p. 98), who states that the atomic weight must be much greater than 174.

It is probable—since these two elements, in common with Th and U, are characterised by the possession of radio-activity—that this will be found to be a property peculiar to the elements of very high atomic weight, and that the occasional occurrence of this property in elements of lower atomic weight, e.g., Ba, Y, Bi, &c., may ultimately be traced to admixture of minute traces of elements belonging to this series.

VOLUMETRIC ESTIMATION OF MANGANESE.

By FRED. IBBOTSON and HARRY BREARLEY.

WE are very pleased to note Mr. Ramage's amended description of the "bismuthate" process for the estimation of manganese in steel works' materials. There is probably no better volumetric process known for the estimation of both large and small amounts of manganese, and none less subject to the interference of uncommon elements than this may be when suitably modified. On this account we wish to extend the usefulness of Ramage's paper by pointing out some sources of error which have escaped his consideration, and some improvement, as we think, in the general application of the process.

Amongst our friends, and by correspondence with Mr. Ramage, we have attempted during the past two years to determine—(1) Which of the two processes described in Reddrop and Ramage's original paper gave the correct result? (2) why the results differed? and (3) some modification of the operations which should be indifferent to this discrepancy, and which should be as little as possible interfered with by the presence of those elements which occur occasionally in steel.

With respect to the first point, "Is the correct result obtained by filtering the oxidised (permanganate) solution into an empty flask and then adding hydrogen peroxide, or into a flask which contains an excess of peroxide to begin with?" We are gratified to find that Ramage has finally come to support our conclusion, viz., that the permanganate should be filtered into an empty flask. But we cannot accept his explanation that, in the original paper, the method of filtering into an empty flask was suggested as an alternative "because we could not be sure of adding a slight excess of hydrogen peroxide to the flask before filtration." At that time Reddrop and Ramage appear to have been unaware that an excess of peroxide, either slight or considerable, suffered any deterioration when the oxidised solution was filtered into it. In fact, in a footnote (*Journ. Chem. Soc.*, 1895, lxvii., 275) they say "the large quantity of ferric nitrate in the filtrate tends to the decomposition both of permanganic acid and hydrogen peroxide, the latter less than the former." Ramage's paper (*CHEM. NEWS*, lxxiv., 209) makes it plain that the statement in this footnote is untrue, and this puts an entirely different complexion on their original paper, more particularly on the comparison they make between Schneider's process for the volumetric estimation of manganese and their own, which is a modification of it.

The different results obtained by filtering into an empty flask, or into an excess of hydrogen peroxide, are properly explained by Ramage to be due to some reaction between ferric nitrate and the peroxide of hydrogen. Nearly a year ago we observed that if the hydrogen peroxide was standardised by adding it to the solution of a steel which had been used for estimating the manganese, the value of the standard was much lower than if it had been titrated alone or in acidulated water; and, in addition to this, the conclusion that the ferric nitrate destroyed a portion of the hydrogen peroxide was supported by numerous series of tests made on the same steel after adding varying steel amounts of peroxide. One series may be given; it will

be seen to agree with Ramage's statement that each c.c. hydrogen peroxide in excess of that really needed corresponds to an error of about 0.01 per cent Mn. The steel used contained 0.32 per cent Mn:—

N/10 H ₂ O ₂ added.	N/10 KMnO ₄ used.	Per cent Mn registered.
3.95	0.60	0.335
6.75	3.20	0.355
11.60	7.60	0.400
18.60	14.10	0.450

To us a defect of this kind in a reagent suggests the advisability of replacing it by some other. But Ramage sticks to the peroxide and minimises the associated error by adding it in small excess only, and depends upon "a slight reduction of the permanganic acid which takes place during and after filtration" to do the rest. The reduction referred to is undoubtedly due to the carbon of the metal having been but incompletely oxidised by the bismuthate in the cold solution; and in very high carbon steels these intermediate oxidation products of the carbon are revealed as a pronounced yellow colour in the filtered solution after an excess of hydrogen peroxide has been added. In such cases the titration with permanganate may be quite unsatisfactory in that the pink colour, on which the end reaction depends, is discharged almost immediately for an indefinite period. This makes it essential to complete the oxidation of the carbon in hot solutions, for high carbon steels at any rate.

In its application to some steel making alloys, and to steels and irons which contain rare elements, but not so rare as to be above notice, the bismuthate process, if hydrogen peroxide is used, either breaks down altogether or does not work very smoothly. We will consider separately steels or alloys which contain chromium, tungsten, molybdenum, titanium, and vanadium.

Chromium.—In the original paper Reddrop and Ramage observe that bismuthate, when added to a nitric acid solution of a chromium salt, very slowly but completely oxidises it to chromic acid. This oxidation is, happily, so slow in cold solutions that all the manganese may be transformed to permanganate without any appreciable amount of chromic acid being formed. Thus a steel containing 0.50 per cent manganese was dissolved along with 14 c.c. N/10 K₂Cr₂O₇. On adding bismuthate, shaking, and at once filtering rapidly, it gave 0.52 per cent Mn; on merely passing the unoxidised solution through a filter already well coated with bismuthate, it gave 0.53 per cent Mn; after standing in contact with bismuthate for five minutes 0.55 per cent Mn, and after ten minutes 0.57 per cent Mn. A long series of steels which have been assayed in other ways also shows that if the solution is kept quite cold the presence of chromium introduces no error unless the contact with bismuthate is extended. Chromium steels which are not completely decomposed by nitric acid are generally got into solution by treating them in the first case with dilute sulphuric, and then adding nitric acid.

Tungsten.—The presence of this element introduces no error; but in steels containing much tungsten, and particularly in chrome-tungsten steels, the precipitate has a tendency to pass the filter. The joint presence of tungsten and hydrofluoric acid (as when ferro-tungstens are opened up with HF+HNO₃) cause the results to be high and very erratic; it is necessary in such cases either to drive off the HF with H₂SO₄, or if the manganese is low to adopt the red-lead process (*CHEM. NEWS*, lxxii., 209).

Molybdenum.—The presence of this element causes the results to be high and erratic.

Titanium and Vanadium.—The use of hydrogen peroxide has this advantage:—A steel or iron containing titanium or vanadium would be distinguished by the characteristic yellow or reddish-brown colour formed on adding an excess of the peroxide. But the disadvantage of its use under the same circumstances may be twofold:—

1. The oxidised titanium or vanadium compound to which the colour is due does not react so readily

with permanganate as hydrogen peroxide does; so that unless the hot solution is treated with bismuthate or by some other means the colour due to organic matter is destroyed, and the end reaction sharpened, there is some uncertainty about hitting the final point. Otherwise the permanganate reacts with the coloured metallic compounds to the same extent as it would with the hydrogen peroxide which formed them, *i.e.*, the difficulty is one of manipulation merely.

2. When much of either vanadium or titanium is present, as in the assay of their ferro alloys, so deep a colour is formed with the hydrogen peroxide that "a slight excess" over and above that needed to destroy the permanganate cannot be gauged, and thus one is prone to commit the very error which Ramage's paper is intended to eliminate.

We work the bismuthate process as follows:—Dissolve 1.1 grms. of the metal in 35 c.c. of 1.20 nitric acid, and then add bismuthate a little at a time to the somewhat cooled solution until a permanganate colour persists, or on boiling is decomposed to manganic oxide. Clear up the permanganate or the dioxide precipitate with a little hydrogen peroxide, sulphurous acid, or ferrous sulphate, free from manganese. Now cool the solution, and add about 10 c.c. of water, and as much bismuthate as leaves a considerable portion undecomposed. Filter into a clean flask, wash with dilute (3 or 4 per cent) nitric acid, add an excess of ferrous ammonium sulphate, and titrate with decinormal permanganate.

The advantages of using ferrous sulphate are that it does not matter how small or great an excess is added since it does not react with the ferric nitrate, and it can be safely used in cold nitric acid solutions of the above strength if the permanganate titration is not needlessly delayed. In the presence of chromium or tungsten this modification of the process is subject to such limitations as apply when hydrogen peroxide is used, but molybdenum, titanium, and vanadium do not interfere. The only indication during the titration that any of these elements are present is noticed with vanadium; then on adding an excess of ferrous sulphate the blue colour of hypovanadate appears if enough (about 0.5 per cent) vanadium happens to be present. When the excess of ferrous sulphate has been decomposed, and the added permanganate is re-oxidised from V_2O_4 to V_2O_5 , the reaction is slower and the end point is not so sharp and clear as when vanadium is absent. This uncertainty, however, need never involve more than one, or at most two-tenths, of a c.c. N/10 permanganate if care has been taken to destroy all the organic matter in the hot solution.

The high price of bismuthate (20s. to 24s. per pound) may retard the general adoption of the process, but it will be found on calculation that this item does not exceed one penny per assay, and is therefore inconsiderable; moreover, the use of 2 grms., as is generally recommended, for the assay of an ordinary steel (particularly if mild) is needlessly extravagant. The economy of the process may be further enhanced when series of everyday steels are being assayed by proceeding as follows:—Pass two or three samples through the same filter; then pour a sample which has been merely dissolved and cooled on to it. A funnel large enough to hold all the ferric solution should be used in order that the bismuthate may be evenly diffused through the liquid by stirring with a glass rod. The filtration should not be accelerated beyond what is necessary to cause the solution to pass rapidly in drops; the results are satisfactory.

By oxidising as usual.	By passing only through filter.
0.62	0.60
2.29	2.25
0.58	0.58
0.68	0.67
0.09	0.10

Bower Road, Sheffield,
November 6, 1901.

VOLUMETRIC ESTIMATION OF MANGANESE.

By LAWRENCE DUFTY.

IN a paper on the estimation of manganese by means of "sodium bismuthate," published by Reddrop and Ramage in the *Journ. Chem. Soc.* in 1895, and just recently reviewed by one of the authors in this journal (*CHEM. NEWS*, lxxiv., p. 209), a colorimetric method for the estimation of very small amounts of manganese is advocated, a solution of permanganate being used as a standard, and the colours compared in Nessler tubes. No doubt is cast upon the accuracy of results obtained by this process, but in applying it to steel analysis one or two modifications produce a more practical method which works equally well for low and high manganese steels; in addition, as the Mn is determined on the nitric acid solution after estimating carbon by colour, a considerable saving in time (required for weighing out, &c.) is effected.

The modified process is briefly as follows:—The nitric acid solution is transferred (after the carbon has been estimated) to a graduated stoppered test-mixer (on foot); the carbon tube being rinsed out into the mixer, and the solution then made up to a definite volume with nitric acid (HNO_3 , sp. gr. 1.20, is used throughout). A standard steel, of known Mn contents, is treated in like manner, being diluted to the same volume as the sample. Equal quantities of "bismuthate" are then added through a dry funnel, and the contents thoroughly mixed; the mixing being repeated five minutes later. After being allowed to settle in a dark cupboard, which usually takes about thirty minutes, measured quantities of the clear pink solutions are transferred by means of a pipette to stoppered carbon tubes, and the colours compared in the usual manner.

In practice it has been found most convenient to weigh out 0.1 gm. of steel, dissolving in 2 or 3 c.c. HNO_3 , according to carbon contents, and after the carbon is estimated transferring to 25 c.c. test-mixers, and diluting with HNO_3 to 20 c.c. if the manganese be under 0.8 per cent, or to 25 c.c. if over that percentage. 0.2 gm. "bismuthate" is then added to each tube, and after mixing and allowing to settle, exactly 5 c.c. are transferred to the comparing tubes, the standard being diluted to a convenient tint for comparison (*e.g.*, 0.82 standard to 16.4 c.c.). The standard used for the carbon estimation may conveniently be used for determining the manganese, and one standard solution will serve for a batch of determinations as in colour-carbon.

The question of the varying strength of acid in the mixer affecting the results was investigated, and the following figures show to what extremes the method may be worked. Steel used contained 0.82 per cent Mn. Each sample was dissolved in 3 c.c. HNO_3 :—

	Diluted with water to— C.c.	Then with HNO_3 (1.20) to— C.c.	Result. Mn.
1.	10	25	(Used as standard).
2.	7.5	25	0.82
3.	15.0	25	0.81
4.	25.0	—	0.82
5.	—	25	0.80

The above modification of the "bismuthate process" has been used by the author and others for some time past, and gives every satisfaction. For steel works with Siemens or Bessemer plant, where a large number of analyses have to be made as rapidly as possible, the advantages of this modification over the original volumetric process are obvious; a considerable saving in time not only being effected, but 90 per cent less "bismuthate" is required for each estimation.

The Laboratory,
Continental Steel Works, Sheffield.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART X.

By HARRY BREARLEY.

(Continued from vol. lxxxiii., p. 310).

ALUMINIUM.

A LARGE number of papers dealing with the estimation of aluminium in phosphatic materials, in which the iron is separated with NaHO, or the Al estimated by difference after determining the Fe volumetrically, are mostly unnoticed, because such processes are in principle very well known, and in steel works practice have only a limited application.

I. SEPARATION FROM OTHER ELEMENTS.

Iron.—

1406. REYNOLDS (C. N., ii., 208).—Add oxalic acid to keep up Al_2O_3 , pour into $\text{AmHO} + \text{Am}_2\text{S}$, oxidise the filtrate, and precipitate the Al with Am_2CO_3 . PISANI (C. N., iii., 257).—Oxalate keeps up the Al_2O_3 only for a time; heat readily causes it to separate.
1407. DYER (C. N., liii., 51).—The ammoniacal citrate solution of the oxides is treated with Am_2S , and the ferrous sulphide filtered off.
1408. CARNOT (C. N., xlv., 85).—Add tartaric acid, and precipitate Fe with Am_2S ; Al is precipitated from the acetic filtrate as AlPO_4 . In order to separate Al from Cr, the latter must be oxidised to CrO_3 .
1409. DEVILLE (C. N., v., 102).—Heat $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ in $\text{H} + \text{HCl}$, and weigh the residual alumina. A similar process is used by L'Hôte (C. N., lv., 176), Koninck (C. N., lxi., 13), and Rozycki (Z. I. S. I., 1893, ii., 414).
1410. GOOCH and HAVENS (C. N., lxxx., 39).—Fe is volatilised and separated from Al in HCl containing Cl at lower temperatures than with HCl alone.
1411. WÖHLER (C. N., xviii., 154).—Boil neutralised solution with thiosulphate to expulsion of SO_2 . Al_2O_3 is precipitated.
1412. PARNELL (C. N., xxi., 54).—To slightly acid solution add "hypo." more than equivalent to free acid, and boil only ten or fifteen minutes.
1413. FLIGHT (C. N., xxxi., 214).—Boil faintly acid solution (containing P_2O_5) for several hours with excess of hypo.
1414. DONATH and JELLER (Z. S. C. I., 1887, 458).—After boiling with hypo., the filtrate should be boiled down one-half to recover small amounts of Al_2O_3 . The precipitate must be strongly ignited in order to get rid of the sulphur.
1415. ESILMANN (C. N., xxviii., 209).—To warm dilute solution, containing free acid and excess P_2O_5 , add hypo. and acetic acid; boil twenty minutes, and collect AlPO_4 .
1416. WARINGTON (C. N., x., 1).—Precipitate the acid solution (of mineral phosphate) with NaHO; digest, and estimate Al in filtrate. Also JONES (C. N., liii., 87), GLADDING (C. N., lxxiv., 146), and many others.
1417. LASNE (C. N., lxxiv., 309).—As 1416. AlPO_4 is soluble in acetic solutions. True AlPO_4 is formed by boiling with hypo. only when a certain excess of P_2O_5 is present.
1418. GLASER (Z. C. S., lxiv., ii., 346).—The mixed phosphates are fused with Na_2CO_3 ; Al can then be completely boiled out with water.
1419. LYTE (C. N., xxviii., 324) and BECKMAN (C. N., xlv., 226).—A boiling solution of $\text{Ba}(\text{HO})_2$ separates Fe and Al perfectly, and so dispenses with the preparation of pure soda, &c.

1420. GLASER (Z. S. C. I., 1897, 936).—To nearly neutral and cold solution add Na_2O_2 until the solution becomes quite clear. Boil to decompose soda ferrate, and filter off $\text{Fe}_2(\text{HO})_6$.
1421. THOMSON (C. N., liv., 252).—Add $\text{Am}\bar{\text{A}}$ to neutral FeO solution containing P_2O_5 . Separate a little Fe from precipitate with NaHO, and estimate as AlPO_4 . If Mn is present, the first separation is made, omitting P_2O_5 . Neither the "NaHO" nor hypo. separation of Al from large amounts of iron is satisfactory.
1422. PARRY and MORGAN (C. N., lxvii., 308).—Mainly as 1421; omitting the P_2O_5 , and precipitating finally as Al_2O_3 .
1423. DONATH (C. N., xlvii., 12).—Reduce with hypo., pour into alkaline KCN, acidify with HCl , and precipitate Al with Am_2CO_3 . Regelsberger (Z. S. C. I., 1891, 1033) precipitates the Al finally by boiling with AmNO_3 .
1424. MOORE (C. N., lviii., 125).—Add excess NaHCO_2 to FeO solution, and then form ferrocyanide by adding to KCN. Boil with AmCl to precipitate Al. Separates also Ni and Co from Al.
1425. BORNTÄGER (C. N., lxvii., 204).—Precipitate oxides together from neutral solution with potassium oleate, and dissolve out the iron oleate with hot petroleum.
1426. VIGNON (C. N., li., 165).—Mix the solution with large excess of trimethylamine, and allow to stand twenty-four hours; the precipitated Al is completely re-dissolved.
1427. HESS and CAMPBELL (C. N., lxxxi., 158).—From neutral and reduced solution precipitate Al (together with all the P_2O_5) with phenylhydrazine. Cr is also precipitated; but neither Fe, Ca, Mg, Mn, Co, or Ni are.
1428. DE KONINCK (C. N., lxii., 19).—Add nitroso-β-naphthol to acetic acid solution; the Fe only is precipitated. See 25 and 26 for other separations with this reagent.
1429. GOOCH and HAVENS (C. N., lxxiv., 296).— Al_2Cl_6 is almost insoluble in etherised HCl ; Fe_2Cl_6 easily soluble. Precipitated Al_2Cl_6 ignited under HgO to Al_2O_3 .
1430. BEILSTEIN and LUTHER (C. N., lxvi., 37).—Evaporate HNO_3 solution on water-bath, and dissolve out basic aluminium nitrate with water.
1431. MARCHAL and WIERNIK (Z. C. S., lxiv., ii., 49).—Neutralise acid solution and boil with freshly precipitated MnO_2 . The filtrate contains Al (and Cr); the Fe remains with the undissolved MnO_2 .
1432. KOHN and WOODGATE (Z. S. C. I., 1889, 260).—Electrolytic separation from oxalate solutions. ENGELS (Z. S. C. I., 1898, 796).—From solution containing Rochelle salt.

Manganese.—

1433. GIBBS (C. N., xi., 102).—By boiling neutral solutions with soda acetate, Al is precipitated free from Mn, Ni, Co, Zn, Mg, Ca, and Ur. A second precipitation is more necessary than in the like Fe separation.
1434. LEFFLER (C. N., lxxvii., 265).— $\text{Al}_2\text{Cl}_6 \cdot 11\frac{1}{2}\text{Al}_2(\text{HO})_6$ may be formed by neutralising Al_2Cl_6 solutions with dilute alkalis. The acetate precipitation separates Mn, but not Ni, quantitatively. The separation of Ni by Na_3PO_4 in acetic solutions is approximately accurate.
1435. Chromium.—BREARLEY (C. N., lxxvii., 179).—Al is not separated from CrO_3 by precipitating with AmHO , Am_2CO_3 , or acetates, and a considerable excess of Na_2CO_3 is needed. It may be separated by Na_3PO_4 in acetic solutions.

Magnesia and Lime.—

1436. WRINKLE (C. N., xxii., 4).—The amount of MgO

which goes down on precipitating Al with AmHO depends on the presence of SO_3 and the mode of adding AmHO.

1437. ROSE (C. N., ii., 291).—By adding AmHO and boiling off excess, any Ca precipitated by CO_2 impurities is re-dissolved if ammonium salts are present.

Copper, Zinc, Mercury, &c.—

1438. HAVENS (C. N., lxxviii., 53).—Cu, Zn, Hg, and Bi are separated as in 1429.
1439. JANNASCH (Z. C. S., lxxvi., ii., 60).—Hg is precipitated by ammoniacal hydroxylamine in the presence of oxalic acid.
1440. Zircon.—DAVIS (C. N., lix., 100).—Zr is precipitated from nearly neutral solutions with soda iodate. Al remains in solution.

Beryllium.—

1441. ZIMMERMAN (C. N., lviii., 49).—Boil with KHO; Be is precipitated. Or boil neutral solution with hypo.; Al is precipitated.
1442. HAVENS (C. N., lxxvi., 111).—As in 1429.

II. GRAVIMETRIC ESTIMATIONS.

1443. PENFIELD and HARPER (C. N., liv., 91).—Some instructive experiments on the precipitation and washing of $\text{Al}_2(\text{HO})_6$.
1444. GUYARD (C. N., xlviii., 119).—Alumina precipitated in the presence of glycerin falls in dense flocks which are easily washed.
1445. LUCKOW (C. N., xi., 205).—Precipitate with bicarbonates rather than carbonates, as the precipitate is less bulky and more easily washed. The smaller excess of AmHO and larger of Am_2S used for precipitating the better. Cochineal colours Al solutions carmine.
1446. ALLEN and GOTTSCHALK (Z. S. C. I., 1900, 1149).—The Al is precipitated as basic carbonate by passing CO_2 into a solution which contains only a small excess of KHO.
1447. MOISSAN (C. N., lxxiii., 49).— Am_2S (with reasons), and not AmHO, is used for precipitating Al. Al_2O_3 is difficult to dehydrate. Estimates also Si, Fe, C, Cu, and Na in Al alloys.
1448. LUNGE (Z. S. C. I., 1890, 111).—On precipitating Al with AmHO, the excess need not be boiled off if AmCl is present; the precipitate retains no SO_3 .
1449. STEAD (Z. S. C. I., 1889, 966).—Dissolve Fe in HCl, separate SiO_2 , and boil nearly neutral solution with Na_3PO_4 and $\text{Na}_2\text{S}_2\text{O}_3$. Dissolve precipitated AlPO_4 in HCl, separate little Fe with NaHO and re-precipitate Al as before. PHILLIPS (C. N., lxi., 313) describes a similar process, and so does CARNOT (C. N., lxi., 10 and 172), except that the AlPO_4 first obtained is purified by re-precipitating in the same way.
1450. OSMOND (Z. I. S. I., 1890, ii., 200).—Heat steel in current of HCl; the Al in the residue is estimated by difference after deducing S and P.
1451. DROWN and M'KENNA (C. N., lxiv., 194).—The steel solution, freed from C and SiO_2 , is electrolysed, using Hg cathode. The Fe forms an amalgam, and the Al is precipitated from filtered solution as AlPO_4 .
1452. SCHÖNNEISS (Z. I. S. I., 1892, ii., 518).—Evaporate HNO_3 solution, fuse evaporated residue with NaHO in silver dish, and precipitate Al from acidulated filtrate with AmHO.
1453. ZIEGLER (C. N., lxvi., 321).—Fuse powder (with or without oxidation by acids), and precipitate as $\text{Al}_2(\text{HO})_6$ after filtering off the iron.
1454. ZIEGLER (Z. I. S. I., 1891, i., 440).—Dissolve Fe in HCl, complete reduction to FeO with hypophosphite, and add excess ZnO. Dissolve precipitate in HCl, and eliminate impurities by pre-

cipitating with AmHO both before and after fusing with soda carbonate.

1455. LEDEBUR (Z. I. S. I., 1893, ii., 534).—Treat strong HCl solution of Fe_2Cl_6 with ether (see 1429). Precipitate Al in aqueous solution as AlPO_4 with Na_3PO_4 and acetate.
1456. KLEMP (C. N., lxii., 241).—Treat Al metal with KHO, burn liberated H to H_2O , and calculate percent Al from increased weight of H_2SO_4 tube.
1457. REGELSBERGER (Z. C. S., lxii., 102 and 535).—Dissolve Al metal in KHO, boil with AmNO_3 , and collect precipitated Al_2O_3 . KHO completely dissolves Al from its Ni or Cu alloy.
1458. REGELSBERGER (Z. C. S., lxiv., ii., 48).—Estimate Al in Fe-Al alloy by process 1423; and gives means of analysing Al-Cu and Al-Zn alloys. JUPTNER (Z. C. S., lxiv., ii., 391) calls 1423 Neuhäusen's method.
1459. THOMSON (Z. S. C. I., 1886, 152).—Precipitate Al and Fe together as phosphates, and determine Fe volumetrically and Al by difference. AlPO_4 becomes basic on washing with H_2O .
1460. MACIVOR (C. N., xxix., 199).—The ignited $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ are dissolved in H_2SO_4 in the presence of zinc prior to the Fe titration.
1461. GLASER (Z. C. S., lxii., 1523).—Precipitation of Al solution containing excess P_2O_5 with AmHO or AmA at 100° gives basic phosphates; at 70° , AlPO_4 exactly is formed.
1462. HUNT, CLAPP, and HANDY (C. N., lxv., 223 and 235).—Analysis of Al metal. Al estimated as AlPO_4 by boiling with hypo.
1463. HANDY (C. N., lxxv., 55, 66, 79).—Estimation of Cu, Fe, Si (total and graphitic), Na, and C in Al. Al_2O_3 is very hygroscopic. Analysis of the Cu, Ni, Mn, Cr, W, Ti, and Zn alloys of Al, Al solders, and the raw materials of Al manufacture.
1464. CAMP (C. N., lxxxii., 91).—In ore and cinders the HCl filtrate from SiO_2 is neutralised and AlPO_4 precipitated by boiling with AmA and hypo. AlPO_4 is slightly soluble in the wash-water.

III. VOLUMETRIC ESTIMATIONS.

1465. REISS (C. N., xlvii., 248).—To boiling acetic solution containing CaCl_2 add standard AmO until a turbidity appears; $3 \text{ AmO} = 1 \text{ Al}_2\text{O}_3$.
1466. PRUNIER (C. N., i., 235).—The neutral solution of Al, using tropæoline indicator, is precipitated by $\text{N}/2$ AmHO, and the excess determined in a fraction of the filtrate.
1467. NEUMANN (Z. C. S., lxviii., ii., 64).—Precipitate with standard alkaline sulphide, add H_2SO_4 to portion of filtrate, and titrate with KHO.
1468. LESCŒUR (Z. C. S., lxxiv., ii., 484).—Make solution neutral to helianthin, add excess of alkali, boil, and titrate back with acid, using phenolphthalein.
1469. BAYER (C. N., lii., 277).—Add NaHO in excess, and titrate with litmus as indicator in one portion and tropæoline in another. ATKINSON (C. N., lii., 311) uses phenolphthalein instead of litmus. See also BAYER (C. N., liii., 40), LUNGE (Z. S. C. I., 1890, 767), CROSS and BEVAN (Z. S. C. I., 1890, 202; and 1891, 314), and E. B. (Z. C. S., i., 651).
1470. KRETZSCHMAR (Z. S. C. I., 1890, 1064).—Add standard Na_3PO_4 and AmA, and determine excess of P_2O_5 with uranium acetate. Any Fe present is estimated with KMnO_4 , and its FePO_4 equivalent deducted.
1471. STOCK (Z. S. C. I., 1900, 277).—On adding KI and KIO_3 to Al solutions, $\text{Al}_2(\text{HO})_6$ is precipitated and I liberated. The I is estimated with hypo, at boiling-point.

(END OF PART X.).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 9th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

We have to record a further serious deficiency in the rainfall at Oxford during the month of October. The actual amount of rain measured was 1.18 inches, fairly well distributed throughout the month; the average fall for the month is 2.76 inches; this leaves a deficit of 1.58 inches, and, added to the previous deficit, 0.92 inch, makes a total deficit of 2.50 inches, or 12 per cent on the thirty-five years' average.

Our bacteriological examinations of 563 samples have given the results recorded in the following table; we have also examined 56 other samples, from special standpipes, wells, &c., making a total of 619 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	173
New River, filtered (mean of 136 samples) ..	4
Thames, unfiltered (mean of 27 samples) ..	865
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 307 samples) ..	13
Ditto ditto highest	315
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	155
River Lea, from the East London Company's clear-water wells (mean of 39 samples) ..	12

Of the 482 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 28 samples, or 5.8 per cent, were sterile. Only one sample contained more than 150 microbes, while only seven samples, or 1.4 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the seven excess samples was 149, against a corresponding mean of 118 in eight excess samples during September.

The remarkable purity of the London water at this time of year is no doubt partly due to the very small rainfall in the valleys of the Thames and Lea.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.
(Continued from p. 239).

PART II.—THE DETERMINATION OF URANIUM.

Determination of Uranium as Oxide.

THE precipitant which Péligot used in 1840 for the estimation of uranium was ammonia, the principal reagent used for that purpose at the present time. The yellow precipitate which forms when ammonia is added to a uranyl solution is hydrated ammonium uranate (*Chemiker Kalender*, 1899, p. 270), $(\text{NH}_4)_2\text{UO}_7 \cdot x\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{O} \cdot 2\text{UO}_3 \cdot x\text{H}_2\text{O}$, which is soluble in alkali carbonate solutions, and slightly soluble in pure water; but in water containing ammonia, ammonium nitrate, or ammonium chloride it is insoluble (Corney's "Dictionary of Chemical Solubilities"). The presence of tartaric acid, oxalic acid, or non-volatile organic substances prevents the precipitation of ammonium uranate (Fresenius's "Qualitative Chemical Analysis," 219).

If the solution contains any alkalis or alkaline earths, a portion of these will be precipitated along with the uranium (Fresenius's "Qualitative Chemical Analysis," Sixth Edition, p. 533).

Berthier's Method (*Liebig's Ann. Chim.*, xlv., 184).—The reagent next in importance to ammonia, for the estimation of uranium, is ammonium sulphide, which was first used (in 1840) by Berthier. A complete precipitation of uranium by ammonium sulphide is obtained, provided the solution is previously nearly neutralised by ammonia, and no carbonates are present. The precipitate which forms is usually black in colour, sometimes changing to reddish-brown (*Pogg. Ann.*, cxvi., 352). When a large excess of the precipitant is added, and it is allowed to stand, the liquid sometimes assumes a brown colour (*Pogg. Ann.*, cxiv., 120). This colour, says Zimmerman (*Liebig's Ann. Chim.*, 1880, cciv., 224), is due to the solubility of uranyl sulphide in ammonium carbonate contained in the ammonium sulphide. When the ammonium sulphide contains a considerable amount of thiosulphate the red sulphide described by Remele (*Pogg. Ann.*, cxvi., 352) is formed; but when thiosulphate is absent only the dark precipitate results. Thiosulphate in the reagent is due to the oxidation of ammonium sulphide by atmospheric oxygen.

In 1865, A. Remele studied the method for the estimation of uranium by the use of ammonium sulphide, and found the best results were obtained by the following procedure (*Zeit. Anal. Chem.*, iv., 379);—The ammonium sulphide should be fresh, and kept well corked, as it absorbs carbon dioxide when exposed to the atmosphere. To the nearly neutral ammoniacal solution, add an excess of yellow ammonium sulphide, and keep the solution near boiling for an hour, in order to convert the $(\text{UO}_2)\text{S}$, which is first formed, into a mixture of UO_2 and sulphur. This precipitate is rapidly dissolved by alkali carbonates and by tartaric acid. It is slightly soluble in pure water, is soluble in dilute, but insoluble in absolute, alcohol. It is readily soluble in acids, even acetic acid (Corney's "Dictionary of Chemical Solubilities," 1896). The presence of ammonium chloride or ammonium nitrate assists the precipitation of $(\text{UO}_2)\text{S}$, as it is less soluble in these solutions. The precipitate, containing all the uranium, is filtered off, and washed with cold or hot water containing a small amount of ammonium sulphide and ammonium chloride or nitrate. Wash first by decantation, and finally on the filter. The precipitate during washing passes to yellow uranic hydroxide. It is dried, then roasted to remove all the sulphur, and finally converted

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xlii., No. 10.

TABLE IV.

(The theoretical amount of uranium taken was 0.1925 grm.).

Expt. No.	Approximate dilution. C.c.	Salts present.	Crucible in which ignited.	Weighted as—	Weight of U_3O_8 .	Uranium equivalent of U_3O_8 .	Ignited in hydrogen for— Hours.	Weight of UO_2 .	Uranium equivalent of UO_2 .
1.	200	NH_4Cl	Platinum	U_3O_8	0.2242	0.19130	—	—	—
2.	200	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	—	—	—
3.	150	NH_4Cl	Platinum	U_3O_8	0.2269	0.19260	—	—	—
4.	150	NH_4Cl	Platinum	U_3O_8	0.2266	0.19235	—	—	—
5.	175	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	2	0.2191	0.19329
6.	175	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	Platinum	$\begin{cases} U_3O_8 \\ UO_2 \end{cases}$	0.2267	0.19243	$\frac{3}{4}$	0.2179	0.19223
7.	175	$\begin{cases} NH_4Cl \\ CHCl_3 \end{cases}$	Porcelain	U_3O_8	0.2269	0.19260	$2\frac{1}{2}$	0.2207	0.19479
8.	150	NH_4Cl	Platinum	U_3O_8	0.2268	0.19252	1	0.2211	0.19505
9.	150	NH_4Cl	Platinum	U_3O_8	0.2270	0.19268	$\frac{3}{4}$	0.2221	0.19593
10.	150	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	Porcelain	U_3O_8	0.2280	0.19353	—	—	—
11.	175	$\begin{cases} NH_4Cl \\ Alcohol \end{cases}$	Porcelain	U_3O_8	0.2270	0.19268	—	—	—
12.	175	NH_4Cl	Platinum	UO_2	—	—	$\frac{1}{2}$	0.2180	0.19232
13.	150	NH_4Cl	Porcelain	—	—	—	1	0.2240	0.19761

TABLE V.—Precipitation of Uranium by Disodium Hydrogen Phosphate.

Expt. No.	Approximate dilution. C.c.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. (UO ₂) ₂ P ₂ O ₇ . Minutes.	Weight of UO ₂ .	Uranium equivalent.	Theoretical amount of uranium taken.
1.	150	$\begin{cases} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{cases}$	$\begin{cases} Cold, then heated to \\ boiling-point \end{cases}$	Platinum	15	0.2875	0.1921	0.1925
2.	150	$\begin{cases} NH_4Cl \\ NH_4C_2H_3O_2 \end{cases}$	" "	"	10	0.2884	0.1927	0.1925
3.	150	$\begin{cases} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{cases}$	" "	Porcelain	10	0.2878	0.1923	0.1925
4.	150	$\begin{cases} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{cases}$	$\begin{cases} Boiling-point for one hour \\ after precipitation \end{cases}$	Platinum	10	0.2851	0.1905	0.1925
5.	150	$\begin{cases} Chloroform \\ NH_4C_2H_3O_2 \end{cases}$	" "	"	10	0.2848	0.1903	0.1925
6.	150	$\begin{cases} NH_4NO_3 \\ NH_4C_2H_3O_2 \end{cases}$	" "	Porcelain	15	0.2875	0.1921	0.1925
7.	150	$\begin{cases} Chloroform \\ NH_4C_2H_3O_2 \end{cases}$	" "	"	20	0.2870	0.1918	0.1925

into U_3O_8 by ignition in the air, or into UO_2 by ignition in a current of hydrogen, and allowing to cool in same.

A complete separation of uranium from the alkalis and alkaline earths is obtained by means of ammonium sulphide (*Zeit. Ann. Chem.*, i., 411).

C. Winkler made a comparison of this method with Péligot's ammonium method (Fresenius's "Quantitative Chemical Analysis," p. 281), and states that the precipitation of uranium by pure ammonium sulphide is trustworthy (*CHEM. NEWS*, 1881, xliii., 153).

Experimental.

Precipitation of Uranium by Ammonia.—For each determination a measured amount of standard uranium nitrate solution was run into a beaker, and enough distilled water added to bring the volume to from 150 to 200 c.c. The solutions were brought to boiling, and a few drops of nitric acid added, and the uranium precipitated by adding an excess of ammonia to the hot solution. The precipitates which formed were a bright lemon-yellow colour, and settled rapidly. The precipitates were allowed to settle, and washed several times by decantation, and twice on the filter with warm dilute ammonium chloride solution (2 grms. salt to 100 c.c. water), after which they were dried in a hot oven, and ignited and weighed as oxides.

Table IV. gives the conditions observed.

U_3O_8 multiplied by 0.84884 gives the uranium equivalent; UO_2 multiplied by 0.88218 gives the same. These are the factors obtained by taking the atomic weight of

uranium as 239.6, and that of oxygen as 16 (*Journ. Amer. Chem. Soc.*, 1901, xxiii., 94).

For all the above precipitations the solutions, of from 150 to 200 c.c. volume, were made decidedly acid with from 0.5 to 1 c.c. nitric acid (sp. gr. 1.42), brought to boiling, and ammonia added in excess. Some of the solutions were boiled for about fifteen minutes after the precipitation by ammonia, while others were filtered directly without boiling. The boiling caused the lemon-yellow coloured voluminous amorphous precipitate to change to a more crystalline form, less voluminous, and of a slightly darker colour. The precipitates which were boiled were much easier to filter and wash, and were less liable to pass through, which usually happened when boiling was omitted.

The presence of chloroform or alcohol (as recommended by some chemists) did not assist the precipitation, but the presence of ammonium chloride or ammonium nitrate was essential. Five to ten grms. were added previous to the addition of ammonia.

Some of the precipitates were ignited separate from the paper, and others without separating from the paper. The results obtained, whether the precipitates were ignited separately or not, were identical, showing that it is unnecessary to ignite the precipitate and the filter paper separately, as is recommended by the German chemists.

When the uranium was weighed as U_3O_8 , the precipitates together with the filter paper were placed in a crucible and slowly ignited till the paper had completely burned; then the ignition was continued for about fif-

teen minutes in a blast-flame, and allowed to cool slowly in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obviating complete oxidation. The results were the same whether porcelain or platinum crucibles were used.

In all directions given in text-books and journals for weighing uranium as oxide, it is recommended that the dry precipitate of ammonium uranate be strongly ignited over a blast lamp to U_3O_8 , and allowed to slowly cool in a gradually decreasing flame and finally in a desiccator. It is then weighed, and as a means of ascertaining its purity for the purpose of control, it is re-ignited in a current of pure hydrogen and reduced to its lower oxide, UO_2 . This was tried, but only in one case was it possible to completely reduce U_3O_8 to UO_2 , even when the ignition in hydrogen was continued for two hours. This time (experiment No. 6) the reduction was brought about by using a platinum crucible, and igniting strongly in a current of pure hydrogen over the hottest blast-lamp that could be obtained. When a porcelain crucible was used in which the ignition was made, the reduction did not proceed so far as when a platinum crucible was used. The reason for this is the fact stated by Roberts-Austen ("Introduction to Metallurgy," 1898, p. 54) as follows:—"Sainte Claire Deville and Troost discovered that hydrogen and hydrocarbons pass through platinum at a red heat." The further reduction of U_3O_8 , when a platinum crucible is used, would seem to indicate that hydrocarbons of the flame play as important a part in the reduction as the hydrogen. It was impossible to obtain a single complete reduction of the precipitate to UO_2 when a porcelain crucible was used, even when the precipitate was not previously ignited. When a platinum crucible was used, and the precipitate not previously ignited in the air, the complete reduction to UO_2 occurred within half-an-hour by igniting it in a current of pure hydrogen over a blast-lamp, and allowing it to cool in an atmosphere of hydrogen over a gradually decreasing flame. The U_3O_8 is a velvety black coloured mass, and the UO_2 a dull brown coloured mass.

For the above reductions ordinary porcelain and platinum Rose crucibles were used. The hydrogen was purified by Schobig's method (*Journ. Prakt. Chem.*, [2], xiv., 289—299), by first passing it through a strong solution of potassium permanganate to remove the hydrides of arsenic, antimony, phosphorus, and carbon; then through a strong solution of caustic soda to remove hydrogen sulphide; and finally through sulphuric acid (sp. gr. 1·84) to remove moisture.

Determination of Uranium as Phosphate.

Review of Method.

The precipitation of uranium by an alkali phosphate has rarely been employed as a means of estimating uranium, because the precipitate which forms is gelatinous and difficult to wash free from alkali. This trouble has been overcome by adapting the method to volumetric means, which is the reverse of the volumetric estimation of phosphoric acid by a standard uranium solution. The uranium in solution as acetate is titrated by means of a standard solution of sodium-hydrogen-ammonium phosphate ($NaHNH_4PO_4$), which is added till a drop of the precipitated solution brought in contact with a drop of freshly prepared solution of potassium ferrocyanide does not give a brown colouration (Mohr's "Lehrbuch der Chemisch-analytischen Titrimethode," p. 521; Dammer's "Handbuch der Anorg. Chemie," 1893, iii., 686).

The quantitative estimation of uranium by means of an alkali phosphate was first suggested by Leconte (Liebig and Kopp, *Fahresbericht*, 1853, p. 642), and later worked out by Pisani (*CHEM. NEWS*, 1862, iii., 211); but owing to the difficulty of filtering and washing the greenish-yellow, slimy precipitate of UO_2HPO_4 , this method has not come into use.

Experimental.

Were it not for the difficulty of washing the uranium phosphate, which is formed by disodium hydrogen phosphate, this method would afford a decided advantage over precipitating it with ammonia, and weighing it as oxide (U_3O_8), because any error would be greatly diminished by weighing as $(UO_2)_2P_2O_7$. U_3O_8 multiplied by 0·84884 gives the uranium equivalent, while $(UO_2)_2P_2O_7$ multiplied by 0·66815 gives the same; so by weighing the uranium as pyrophosphate the error or loss is decreased.

This method was studied, and the best conditions for weighing uranium as uranyl pyrophosphate were worked out, the results of which are tabulated (see Table V.).

These determinations were made by measuring 50 c.c. of standard uranium nitrate solution into a beaker, diluting to 150 c.c., and adding nitric acid (sp. gr. 1·42), varying the amount from 0·5 c.c. to 1·5 c.c. The solutions were brought to boiling, and ammonia (sp. gr. 0·90) added to neutral reaction and a measured amount in excess—from 1 c.c. to 10 c.c. The yellow precipitate of ammonium uranate was dissolved by adding 50 per cent acetic acid till the precipitate disappeared, and then an excess varying from 1 c.c. to 5 c.c. To the solution—which contained besides uranium acetate, an excess of acetic acid, ammonium nitrate, and ammonium acetate—an excess of a saturated solution of disodium hydrogen phosphate was added. The precipitate which formed was greenish-white in colour, and voluminous. The solution was brought to boiling, then allowed to cool, and filtered. In experiments Nos. 4 to 7 the solutions were kept for one hour on water-baths at the temperature of boiling water, after which they were allowed to cool, then filtered. This treatment assisted the settling of the precipitate, but did not change its gelatinous character.

The washing of the precipitates was done by four decantations, and twice on the filter with a hot dilute solution of ammonium chloride (2·5 grms. of salt to 100 c.c. of water). The washing was not so easy as the ammonium uranate precipitates, even when as much as 5 grms. of ammonium chloride were added to the solution previous to its precipitation. Neither the addition of chloroform nor of ammonium chloride had any effect on the appearance of the precipitate, as there were already sufficient ammonium salts present, formed by the neutralisation of nitric acid by ammonia, and of ammonia by acetic acid.

The precipitates, after washing, were dried at a temperature of from 100° C. to 115° C., separated from the filter-paper, which was first ignited in the crucible, then the precipitate added, and the ignition continued for from ten to twenty minutes at "redness" over a Bunsen burner. The residue in most cases was green in colour, due to the partial reduction of uranyl pyrophosphate. Whenever the temperature of ignition was above "redness" a reduction always occurred, especially when a platinum crucible was used. When a porcelain crucible was used the ignition could be done at "redness," but above this temperature (as over a blast-lamp) reduction always resulted.

The reduced uranyl pyrophosphate was not weighed as such, but was moistened with a few drops of nitric acid (sp. gr. 1·42), dried over a low flame, and re-ignited at "low redness," over a Bunsen burner. The mass after such treatment was always of a lemon-yellow colour. The weight of the yellow uranyl pyrophosphate remained constant, no matter how long it was ignited at a temperature not exceeding "low redness," but above this temperature it always lost weight, and assumed a green colour. Whenever this occurs it may be re-oxidised by treating it with nitric acid, and re-igniting at "low redness."

This green residue of pyrophosphate most probably has the composition $U_2O_3 \cdot P_2O_7$, which is indicated by the weights of several which varied from 0·2820 to 0·2827 grms. 0·2820 multiplied by 0·6853 gives 0·1929 grm. uranium, the theoretical amount of uranium being 0·1925 grm.

One of the residues which was more intensely ignited than the others, with the cover on the platinum crucible, was of a reddish-brown colour. Its weight was 0.2800 grm., showing that the reduction had gone further than $U_2O_3 \cdot P_2O_7$.

The composition of the lemon-yellow coloured uranyl pyrophosphate is $(UO_2)_2P_2O_7$.

(To be continued).

THE ACTION OF SODIUM THIOSULPHATE ON SOLUTIONS OF METALLIC SALTS AT HIGH TEMPERATURES AND PRESSURES.*

By JOHN T. NORTON, Jun.

THE use of sodium thiosulphate as a substitute for hydrogen sulphide in effecting precipitations, and its application in the case of arsenic, antimony, copper, and platinum, was suggested by Himly (*Liebig's Ann. Chem.*, lxiii., 150) before the middle of the last century. Thirteen years later Vohl (*Liebig's Ann. Chem.*, xcvi., 237), and Slater (*Chemical Gazette*, 1855, p. 369), independently, drew attention to this use of sodium thiosulphate, and extended the investigation to salts of tin, mercury, silver, gold, lead, bismuth, and cadmium. Slater, in addition, studied the action of sodium thiosulphate upon chromic acid, molybdates, ferrous and ferric ferrocyanides, ferric sulphocyanide, and potassium permanganate. Following out these lines, the precipitation of copper, together with arsenic and antimony, by treating with sodium thiosulphate the hot solution containing sulphuric acid, and the separation of these elements from tin, zinc, iron, nickel, cobalt, and manganese, has been advocated by Westmoreland (*Journ. Soc. Chem. Ind.*, v., 51); and quite recently Faktor (*Centralblatt*, 1900, ii., 20, 67, 239, 594) has studied the action of sodium thiosulphate upon neutral salts of several of the elements mentioned, as well as the modifying influence of ammonium chloride and other salts upon the course of the reaction.

Subsequently to the work of Himly, Vohl, and Slater, Chancel (*Comptes Rendus*, xlv., 987) developed his well-known method for the precipitation of aluminum as the hydroxide and its separation from salts of iron, by boiling with sodium thiosulphate, the nearly neutral solution, containing the salts of aluminum and iron, at suitable dilution; and upon an extension of the principle of Chancel's separation of aluminum from iron, Stromeyer (*Liebig's Ann. Chem.*, cxiii., 127) founded his well-known processes for the separation of titanium and zirconium from iron. The latter process appears to be fairly trustworthy; but of Chancel's method, although it has met with wide acceptance, it was shown by Wolcott Gibbs very soon after its announcement (*Zeit. Anal. Chem.*, iii., 389) that it fails to bring about complete separation of alumina within a reasonable period of boiling, and this result has been confirmed by Zimmerman ("Inaug. Diss.," Berlin, 1887), who has shown that the boiling must be continued fifteen hours in order to complete the precipitation of the alumina.

It was shown by Dr. Gibbs that when the treatment of salts of aluminum by thiosulphate was carried on in sealed tubes under pressure at $120^\circ C.$, the precipitation of alumina was complete, and further that the precipitation of sulphides of nickel, cobalt, and iron, though partial under ordinary atmospheric pressure, was made complete by heating in sealed tubes to $120-140^\circ C.$

In repeating the experiments of Dr. Gibbs qualitatively and extending them, I have made use of the well-known Pfungst tube to secure the necessary pressure. In each experiment a test-tube containing the mixture of an excess of sodium thiosulphate with the salt whose action was

TABLE I.—Action of $Na_2S_2O_3$ on Salts under Pressure.

Salts used.	Precipitates.	Degree of precipitation.
	<i>Sulphides.</i>	
NiSO ₄	NiS + S	Complete.
CoSO ₄	CoS + S	"
FeCl ₃	FeS + S	"
ZnSO ₄	ZnS + S	"
PbO ₂ (C ₂ H ₃ O) ₂	PbS + S	"
Hg(NO ₃) ₂	HgS + S	"
AgNO ₃	Ag ₂ S + S	"
CuSO ₄	CuS, (Cu ₂ S), + S	"
CdSO ₄	CdS + S	"
K ₂ SbC ₄ H ₂ O ₇	Sb ₂ S ₃ + S	"
Bi(NO ₃) ₃	Bi ₂ S ₃ + S	"
	<i>Hydroxides.</i>	
NH ₄ Al(SO ₄) ₂ ·12H ₂ O	AlO ₃ H ₃ + S	"
K ₂ Cr ₂ O ₇	CrO ₃ H ₃ + S	"
K ₂ ZrF ₆	ZrO ₂ H ₄ + S	"
K ₂ TiF ₆	TiO ₂ H ₄ + S	"
Th(NO ₃) ₄	ThO ₄ H ₄ + S	"
	<i>Elements.</i>	
SeO ₂	Se + S	"
TeO ₂	Te + S	"
	<i>Sulphides.</i>	
MnSO ₄	MnS + S	Partial.
AuCl ₃	Au ₂ S + S	"
(NH ₄) ₂ MoO ₄	MoS ₃ (?) + S, red liquid	"
	<i>Hydroxides.</i>	
BeCl ₂	BeO ₂ H ₂	"
	<i>Undetermined.</i>	
(NH ₄) ₂ U ₂ O ₇	Black	"
K ₂ PtCl ₆	Grey reddish brown liquid	"
CeCl ₃	White-yellow liquid	"
CaCl ₂	" "	"
SnCl ₂	" "	"
BaCl ₂	" "	"
MgSO ₄	—	Trace.
NH ₄ VO ₃	Brown liquid	"
H ₂ KAsO ₄	—	"

studied was placed within the Pfungst tube containing some water; the cover of the latter was set in place, and firmly bolted upon a washer of lead, and the whole was submitted to temperatures varying from 140° to $200^\circ C.$ for an hour by immersing in a bath of paraffin. After cooling, the test-tube was taken out, the precipitate was filtered off, and the filtrate tested by appropriate reagents to determine the completeness of precipitation. The following table records the details of these experiments:—

A perusal of this table brings to light several interesting facts. It appears that salts of nickel, cobalt, iron, zinc, lead, mercury, silver, copper, cadmium, antimony, and bismuth are completely precipitated as sulphides by sodium thiosulphate under the prevailing conditions of temperature and pressure. In the case of manganese precipitation is only partial, and arsenic does not seem to be precipitated from an arsenate without the addition of acid. Tin, curiously enough, is not thrown down as the sulphide from a stannous salt, but gives a dirty white precipitate of uncertain composition. Salts of aluminum, chromium, titanium, zirconium, and thorium are completely precipitated as the hydroxides; but in the case of beryllium, which one would expect to act similarly, the precipitation as the hydroxide is incomplete. Salts of selenium and tellurium are reduced, and the elements are precipitated. The precipitates obtained with barium, strontium, and calcium were white in a bright yellow liquid, but no study was made of the constitution of precipitate or liquid. In the case of magnesium there was no precipitate. Salts of

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xii., No. 68.

molybdenum, vanadium, and uranium gave dark coloured liquids. Thallium yielded a white spongy mass which on compression was reduced to a very small bulk without disintegrating. Salts of gold and platinum gave slight dark precipitates, presumably sulphides, surrounded by dark coloured liquids.

The apparatus used in these experiments and described above is easily handled, and answers sufficiently well for qualitative purposes. But, obviously, the introduction into precipitates of foreign matter caused by the action of water on the glass of the test-tube and porcelain lining of the Pfunst tube precludes the possibility of an exact quantitative study of the reactions involved. For the subsequent experiments, therefore, conducted upon the same general lines, a digester with an interior cylindrical cavity of about 12 c.m. in depth by 5 c.m. in diameter, and provided with a pressure gauge, was employed. As a container for the solutions to be tested use was made of a platinum cylinder 4 c.m. in diameter and 10 c.m. deep, provided with a loose cover. With this apparatus the following quantitative experiments, which deal with those elements which are precipitated as hydroxides, namely, aluminium, beryllium, chromium, zirconium, and titanium, were made:—

In each case a weighed quantity of the salt taken for the experiment was dissolved in 50 c.m. of water in the platinum vessel, and to this a known amount of sodium thiosulphate was added. The vessel was placed in the digester, and the latter was heated by a Bunsen burner in the customary way until the required pressure was shown on the gauge. The apparatus was then cooled, and the platinum vessel removed from the digester. The precipitate was filtered off on ashless paper, ignited, and weighed.

(To be continued).

NOTICES OF BOOKS.

The Chemical Essays of Charles William Scheele. Translated from the *Transactions of the Academy of Sciences at Stockholm*, with additions. With a Sketch of the Life of Karl Wilhelm Scheele, By JOHN GEDDES M'INTOSH. Re-issued by Scott, Greenwood, and Co., 19, Ludgate Hill, London, E.C.

The first English publication of these essays was in 1786, the year Scheele died, and the preface to that early work is given in full; except for some references to Phlogiston and to the works of "Mr. Cavendish" and "Mr. Lavoisier" one can scarcely realise that it was written more than a century ago. In one direction, at all events, things have altered for the good; the then writer, Thomas Beddoes, laments "the very slow and imperfect manner in which the improvements in literature and science, that are made in several countries abroad, become generally known in England," and he recalls many names among the philosophers of Germany and Sweden in particular with whose contributions to the sum of human knowledge

"the authors and professors of Britain, how confident soever of their own superiority, might find it no disadvantage to be better acquainted than they in general appear to be!"

Nous avons changé tout cela! In point of fact, at the present time the *Comptes Rendus* and the *Zeitschrift* are more accessible to the rank and file of English men of science than are the *Philosophical Transactions of the Royal Society*.

The author of the present edition has entered upon his task with an enthusiasm worthy of the subject, and the "Life of Karl Wilhelm Scheele" carries us vividly back to the times when the humble apothecary in the midst of his struggle for a livelihood found time to pursue truth for its own sake.

A glance at these essays shows at once that Scheele's great power rested in the author's painstaking investigation of minute details. Nothing was guessed at; experiment after experiment was "tried until the sought for truth stood out clearly before the toiler." Hampered as he was by the meagreness of chemical knowledge at the time his achievements are little short of marvellous. In his essays on manganese it is clear that he really discovered chlorine, although he called it dephlogistigated muriatic acid, for if we substitute hydrogen for phlogiston we get dehydrogenised muriatic acid; in a word, chlorine. Scheele found a true friend in Bergmann, of whom it was said "the greatest of Bergmann's discoveries was the discovery of Scheele."

The achievements of this indefatigable chemist are too numerous to recount. Among the most prominent are the discovery of glycerin, citric, malic, oxalic, and gallic acids, arsenate of copper (Scheele's green), and sulphuretted hydrogen. His work on the action of light and heat upon silver, on ether, prussian blue, milk, and sugar of milk, carry us back to the days when the chemical world was young, and we wonder to what heights he would have risen had it been his fortune to have lived a century later.

For the collection and arrangement of the essays and the sketch of the life of this remarkable man we offer the author our hearty congratulation, and would recommend the book as a refreshing recreation to the hard-worked student or investigator of the present day.

Notes on Essential Oils, with Special Reference to their Use, Composition, Chemistry, and Analysis. By T. H. W. IDRIS, F.C.S. With Tables of Constants of the more commonly occurring Oils. Second Edition. London: Idris and Co., Pratt Street, Camden Town,

THE first edition of this practical and useful little book appeared about three years ago, and was so well received that the author has felt justified in bringing out a second edition. Much new matter and recent formulæ have been added, but the character of the work, that of a laboratory note-book, remains the same. For fuller information the reader is referred to standard text-books, particularly one that has recently appeared, by E. J. Parry, from whose work the author gives, in the form of an appendix, "a table of constants of the more important essential oils," including source, yield per cent, specific gravity, optical rotation, and constituents.

The book will undoubtedly maintain its reputation for usefulness to analysts and manufacturers. There is both a table of contents and a good index.

A Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing. By CHRISTOPHER RAWSON, F.I.C., F.C.S., Consulting Chemist to the Behar Indigo Planters' Association, co-author of "A Manual of Dyeing"; WALTER M. GARDNER, F.C.S., Head of the Department of Chemistry and Dyeing, Bradford Municipal Technical College; and W. F. LAYCOCK, Ph.D., F.C.S., Analytical and Consulting Chemist. London: Charles Griffin and Co., Limited, Exeter Street, Strand, W.C.

THE work has been prepared as a companion to Mr. Rawson's "Manual of Dyeing," published in 1893. It comprises a general description of dyes, mordants, and other substances employed in dyeing and calico printing, with methods of examining and assaying these various bodies; also descriptions of apparatus and instruments used. The object of the authors has been to produce a book that would be of practical use in the laboratories of colour chemists, &c. Some of the subjects are considered in great detail; for example, the article on indigo occupies over 30 pages, while that on soap includes its composition, properties, manufacture, analysis, deter-

mination of melting and solidifying points, &c. Naturally, the coal-tar products receive a large share of attention. A. G. Green's scheme for the analytical determination of coal-tar dyes is given in full. There is also a good article on "The Analysis and Estimation of Arsenic in Textile Fabrics."

Arranged as a dictionary in alphabetical order, there is no index, but it is well printed, and occupies some 370 pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 18, October 28, 1901.

Chemical Reactions due to Radium.—M. Berthelot. —The author makes a series of experiments on a specimen of radium obtained from M. Curie. He compares certain specific chemical reactions, which are caused by light and by an electric current, to those reactions capable of being provoked by radium. These experiments are tedious, because of the very small quantities of radium able to be used and the necessity of working in glass envelopes. These latter absorb part of the rays, and, in certain cases, probably the most efficient portion; and they are also unsatisfactory on account of the long time necessary to accomplish these phenomena. The experiments tried were—(1). *The Action of Radium on Iodic Acid (I_2O_5) in Darkness.*—After nine days the acid begins to be tinted with violet, and after some time iodine vapour is apparent. (2). *Monohydrated Nitric Acid (HNO_3).*—At the end of two days the acid begins to discolour, whilst if kept for three years in total darkness it is still colourless. (3). A solution of octahedral sulphur in carbon disulphide, when exposed to light, deposits insoluble sulphur in virtue of an exothermic reaction; a tube of radium immersed in the solution in darkness produces no such effect. (4). Gaseous acetylene is very sensitive to the action of the electric current, an exothermic polymerisation taking place. This gas is not affected by either solar light or radium. (5). The slow oxidation of oxalic acid which takes place in presence of light, also takes place in the presence of radium.

Heat Evolved during the Reaction between Free Oxygen and Potassium Pyrogallate.—M. Berthelot. —During a course of electrolytic experiments, the author was led to measure the heat evolved during the action of free oxygen on pyrogallol in presence of potash. He dissolved the substances in molecular proportions and used equal volumes of the solutions. Through this mixture a current of oxygen was passed for some minutes. When $O = 16$ gr., heat absorbed was $+60.2$ cals. Continuing the reaction, a second quantity ($O = 16$ gr.) gave $+50.0$ cals. During the third experiment, $+56.0$ cals. was the number obtained. After this the absorption became too slow to carry on further measurements.

Separation of Iron.—Paul Nicolardot. —In 1859 Béchamp established the existence of soluble ferric oxychlorides to which he attributed the formula $Fe_2Cl_6(Fe_2O_3)_n$. These compounds have an acid reaction, and in them it is impossible to detect either Cl or Fe by their usual reactions. Their sulphates are insoluble. Wyruboff and Verneuil showed later that such compounds apparently exist for the metals of the rare earths, and that they form acid compounds of oxides, more or less condensed, whose sulphates are insoluble. The author revises Béchamp's work, and attempts the quantitative separation of the iron from such a compound. When a solution of neutral Fe_2Cl_6 is heated the liquid becomes

darker, and if a boiling solution of a sulphate is added to this, a precipitate of a sulphate of condensed iron oxide is formed, whose composition varies according to the temperature and according to the dilution. If the sulphate of any metal, such as Mg, Zn, Cu, Ni, Co, Mn, Cd, Cr, Al, or ferrous sulphate is contained in the solution, the precipitate of iron contains no traces of the other metals.

Minimum Value of the Total Heat of Combination, Q.—M. de Forcrand.—The relation already given by the author (*Comptes Rendus*, cxxii., p. 881) can be written
$$\frac{L+S}{T} = \frac{(l+s)M}{T'} = \frac{Q}{T'} = \frac{L+S+q}{T'} = 30; Q \text{ being the sum of } L, S, \text{ and } q.$$
 From this relation various consequences follow directly. (1). At the moment of separation $\frac{L+S}{T} = 30$

and $\frac{L+S+q}{T'} = 30$; also $\frac{q}{\theta} = 30$. θ being here the difference $T' - T$; θ and q are always positive. (2). When q tends towards zero, θ does likewise, and the relation $\frac{L+S}{T} = 30$ again becomes apparent. It results, there-

fore, that the total heat of combination, Q, has for an inferior limit precisely L+S. The author has measured this for certain bodies.

Copper-aluminium Alloys.—Léon Guillet. —The author applies to copper-aluminium alloys a method which he has already described for those of tungsten and aluminium, and for those of molybdenum and aluminium. He was able to isolate the compounds of copper and aluminium predicted by the curve of fusibility and by metallographic researches. Three of these were obtained, corresponding to the formulæ Cu_3Al , $CuAl$, and Al_2Cu . The compound $CuAl$ being obtained mixed with 2 to 3 per cent of a silicide of copper and aluminium.

Qualitative and Quantitative Determination of Traces of Antimony in presence of a Large Proportion of Arsenic.—G. Denigés.—The classical methods do not allow of the determination of very small quantities of antimony, especially in presence of relatively large quantities of arsenic. The author devises a method which allows of the estimation and detection of a thousandth of a milligram, and even less, even when mixed with 500 times the quantity of arsenic.

No. 19, November 4, 1901.

Electrolysis of Ammonium Chloride Dissolved in Liquefied Ammonia.—Henri Moissan.—The electrolysis of ammonium chloride dissolved in liquid ammonia is performed in a glass vessel containing platinum electrodes. The ammonia gas is completely dried and freed from all possible impurities. When a current of 115 volts, and 30 ampères passes, no gas is evolved at the electrodes. After solution of the chloride the current easily passes, and gases are quickly evolved at the poles; chlorine being deposited at the positive pole, which colours the mass yellow. At this temperature, -60° to -80° , no nitrogen is evolved, and no new ammonium chloride, as when the reaction takes place at ordinary temperatures, $4NH_3 + 3Cl = N + 3NH_4Cl$. Hydrogen gas is evolved at the negative pole, and this is proved to be unmixed with other gases. The author shows satisfactorily that this difference in the reaction is merely due to the low temperature.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Society of Arts, 8. (Cantor Lectures). "The Chemistry of Confectioners' Materials and Processes," by W. Jago, F.C.S., F.I.C.

WEDNESDAY, 27th.—Society of Arts, 8. "Leather for Bookbinding," by J. Gordon Parker, Ph.D.

CHEMICAL AND PHYSICAL APPARATUS TRADE.

Wanted, Senior Assistant; also Junior.—State age, experience, and salary required, to Philip Harris & Co., Ltd., Birmingham.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2192.

THE SYSTEMATIC CHEMICAL TREATMENT OF RAGS FOR PAPER-MAKING.

By CLAYTON BEADLE.

THE treatment of rags is almost universally looked upon, not only by the manufacturer, but also by the chemist responsible for their chemical treatment, as being entirely of an empirical order. Manufacturers do not regard such a material as rags as being amenable to any scientific treatment, although the manufacture of sulphite and soda wood-pulp is carried out in the most systematic and scientific manner. Having paid a great deal of attention to rag treatment for paper-making I have been led to the opposite conclusion. I am therefore writing this article with the object of showing that rags of all qualities, in spite of their peculiar nature and irregularity of composition, are amenable to as exact control and scientific treatment as almost any ordinary commercial product.

The difficulties that manufacturers of paper have to contend with are numerous. Although rags are purchased under well recognised trade names, the quality of each grade depends upon the idiosyncracies of each individual dealer. The dealer in turn is largely the victim of circumstances, as one might well infer from the fact that rags are merely the rejecta of civilisation. Each consignment must be carefully examined and valued on its own merits, independently of the trade name by which it is known. The paper-maker has then to sort the various rags he receives into twenty or thirty different qualities. By this means he is able to obtain fairly uniform qualities.

The chemical treatment of rags is merely for the purpose of removing the extraneous matter. This extraneous matter may best be described as consisting of all the dirt "that flesh is heir to." With these difficulties to face, it is hardly to be wondered at that the paper-makers make little use of scientific methods, and rely almost wholly upon their old rule-of-thumb methods and every-day observations.

The conditions under which rags are now treated in the best mills have been arrived at only after many years of observation. As good, if not better, results might have been arrived at after as many months almost, by pursuing a scientific method of investigation. In the ordinary method of procedure, rags of a given quality are dumped into a boiler with what is considered sufficient soda liquor, and, after a certain number of hours of treatment under steam pressure, the rags are washed and removed. If the result is considered good enough the conditions are repeated, but if the result is in any way unsatisfactory, one or other of the conditions is varied. It takes years by this plan of procedure to arrive at a point where no further improvement can be noticed.

The following is a practical and rapid procedure for arriving at the best conditions for boiling rags with soda which can be carried out by any ordinary works chemist:—One quality of rag is taken for investigation. The rags are filled into the boiler with a known quantity of soda. The capacity of boiler, the weight of rags, and the volume of liquor are noted. The charge should be as much as the boiler will take when "trodden in" after the liquor is added. The liquor should be just sufficient to insure complete saturation of rags, but no more. The time of bringing boiler to full pressure is noted. Samples of liquor are withdrawn every hour, and tested for "free" soda, and the boiling is continued until the free soda remains practically constant. The total soda is determined in the first and last sample, and in the case of a

boiler heated with a steam-coil the total soda should remain constant throughout the boiling. When the rags are washed and removed from the boiler a sample is kept for comparison.

A second boiling is conducted on the same lines, but using soda only slightly in excess of that found to be consumed in the first trial. The boiling is continued until the free soda remains constant. The boiled rags should then be compared with the first trial, and the result should be practically the same. In order to ascertain the loss during treatment, ten pounds of rags, which must be so selected as to represent absolutely the bulk, are tied up in a loose bag made of coarse cheese-cloth. This bag is reclaimed after the boiling, and the contents of the bag are bone-dried, exposed to the air to air-dry, and weighed. From this the loss during boiling is calculated.

The examination of liquors taken during the boiling, to avoid unnecessary calculation and work, are treated as follows:—The liquor from each hour is placed in a marked bottle. The bottles are fitted into rough wooden boxes resembling cruet-stands, with leather straps for handles, which can easily be transported. Each box contains a series of bottles sufficient for a boiling. By this means samples from half a dozen boilings can be transported from boiler-house to laboratory by the chemist in one journey. From each sample 32 c.c. is withdrawn by means of a pipette made to measure this quantity. This is titrated with normal sulphuric acid until it no longer shows alkalinity when a drop is placed on a perfectly neutral non-absorbent litmus-paper. On account of the colour of liquor no indicator can be used in solution. For determination of total soda, 32 c.c. is evaporated down in a platinum dish, ignited, and the charred mass wetted with water, and again ignited. The soda can then be dissolved out with water and titrated without filtration in presence of methyl-orange. The readings on pipette give the percentage of Na_2O by dividing by 10. This method of determining the free and total soda has been checked by evaporating a quantity of the liquor to a solid mass, and examining for "free" soda by the method of "salting out." The two methods give almost identical results:—

Dilute liquor tested

as above		28.5 per cent of total soda "free"
Concentrated	and	
"salted out"	.. 26.9	" " " " "

When once the conditions of boiling are fully established check tests can be done from time to time in a more simple manner, as follows:—A portion of the first and last sample is mixed in equal volumes, from which 32 c.c. is withdrawn, and total soda determined. Such quantity of each sample is then drawn off as to give reading on burette which, when divided by 10, represents percentage of "free" on "total" soda, without further calculation. The results are finally expressed in percentage of "free" soda on "total" soda. By examination of these figures the exact behaviour during boiling can be ascertained. I have found, moreover, that still further can be learned by plotting curves showing the diminution of "free" soda per hour during boiling, expressed as percentage on total "soda" present. The accompanying table shows the conditions arrived at after pursuing the mode of procedure above indicated. It must be remembered that no two mills have the same requirements, and there is no regular plan of procedure common to them all or to the majority of them. Furthermore, the different grades of rags in one mill are not comparable with those in another. The table cannot, therefore, be used as a guide for general practice, but merely as showing the mode of expressing the different factors of boiling, and by comparing them with curves constructed as above indicated an idea can be arrived at as to how the conditions influence the rate of absorption of soda. Curve No. 1 should show the absorption of soda per hour of different qualities of rags when treated under the conditions as shown in table. A dotted curve should be constructed from the mean of these. Curve No. 2 should

were washed out with hot water, made up to 200 c.c., 20 c.c. concentrated hydrochloric acid added, and the mixture then heated in a flask fitted with a reflux tube on the water-bath for three hours. At the end of this operation, the mixture was quickly cooled under water, nearly neutralised with caustic soda, and made up to 500 c.c. From this, 50 c.c. were pipetted off and run into a boiling solution containing 60 c.c. Fehling's solution diluted with 60 c.c. water, and the whole boiled for three minutes. The precipitated cuprous oxide was then filtered off by means of an Allihn's filter-tube, washed with water, then alcohol and ether, dried at 110° , and heated in a current of hydrogen. From the weight of copper found, the amount of starch was calculated by E. Wain's table ("König, Unters. d. Landw. Stoffe," p. 750). In another 3 grms. the nitrogen was determined by Kjeldahl's method, using a mixture of sulphuric acid and phosphorus pentoxide, together with a little mercury for the oxidation. For the analysis of the mineral constituents, the ash obtained by incinerating 25 grs. of the dried substance was dissolved in dilute hydrochloric acid and made up to 250 c.c. with water, and in 50 c.c. of this the potash was found by first removing the sulphates with barium chloride, then precipitating the metals other than potassium, sodium, and ammonium compounds with ammonia and ammonium oxalate, filtering, the filtrate evaporated to dryness, and heated gently to volatilise the ammonium compounds. The residue was then treated with hot water, filtered, and to the filtrate an excess of platinum chloride added, and the liquid evaporated again to dryness and the dried residue triturated with alcohol and brought on to a filter, and the residue washed with 95 per cent alcohol till the filtrate ran through colourless; it was then washed through by hot water into a weighed platinum basin, evaporated to dryness, and dried at 110° C. From the K_2PtCl_6 found, the amount of potash (K_2O) present was calculated. In 100 c.c. of the ash solution, the phosphoric acid was estimated by first precipitating with ammonium molybdate, filtering, dissolving the yellow precipitate in dilute ammonia, and precipitating finally with magnesia mixture.

In the remaining 100 c.c. the lime was estimated by the oxalate method after removing the phosphoric acid with sodium acetate and ferric chloride.

The following is the summary of results obtained:—

	1. Unmanured.	2. Twenty tons farmyard manure.	3. Five cwt. superphosphate, two cwt. muriate of potash, and two cwt. sulphate of ammonia.
H ₂ O	76.24	78.08	75.95
Dry matter ..	23.76	21.92	24.05
Starch	17.762	13.557	17.142
Ash	0.967	0.973	0.964
CaO	0.025	0.022	0.028
N	0.506	0.516	0.493
P ₂ O ₅	0.124	0.147	0.121
K ₂ O	0.628	0.635	0.630

The above results show very slight difference between the unmanured and plot manured with artificials, which was anticipated when it was seen that the manurial salts used were still in the undissolved form. Whether this really was the cause of the similarity in composition or truly represents effect of high manuring is still then an open question; but the amount of water and starch in the potatoes manured with farmyard manure differs very much from the amounts in the unmanured ones, and one would expect that, with increased manuring, especially with artificial manures, this difference would be much greater.

The experiments will be repeated next year, since the results obtained at present are not sufficiently certain to give a correct opinion on the subject.

The Agricultural College,
Holmes Chapel.

THE CHEMICAL SOCIETY.

THE following is a copy of the Memorial recently sent to the President of the Chemical Society, together with a complete list of signatories thereto:—

TO THE PRESIDENT OF THE CHEMICAL SOCIETY.

SIR,—We, the undersigned Fellows of the Chemical Society, respectfully request you to summon an Extraordinary General Meeting of the Society, at the earliest possible date, for the purpose of—

- (1) Proposing a modification of By-Law XI., and
- (2) Submitting a resolution.

We subjoin the terms of the proposed modification and resolution, and have the honour to remain,

Yours very faithfully,

(Signed)

T. H. Page.	J. W. Hinchley.
E. C. Jee.	C. E. Browne.
E. Goulding.	F. F. Renwick.
T. A. Henry.	Albert Cooper.
G. S. Blake.	B. V. Storr.
F. B. Power.	P. Gerald Sanford.
H. A. D. Jowett.	H. R. le Sueur.
G. T. Moody.	S. J. Peachey.
W. A. Davis.	W. A. Wayland.
G. Bousfield.	A. W. Harvey.
E. Horton.	H. F. Fermor.
H. B. Redman.	A. H. Coote.
J. Moir.	A. C. Chapman.
W. J. Kemp.	C. E. Beadwell.
G. S. Newth.	E. Neumann.
G. T. Morgan.	H. Bailey.
J. C. Philip.	F. H. Carr.
Chapman Jones.	E. Haynes Jeffers.
A. J. Bullen Cooper.	T. FitzGibbon.
W. Robertson.	J. Wilson.
C. A. West.	W. T. Gilles.
W. H. Merrett.	A. Guthrie.
H. C. H. Carpenter.	W. P. Draper.
E. O. Courtman.	A. Lapworth.
F. Stanley Kipping.	D. Northall-Laurie.
H. H. Robins.	J. T. Hewitt.
W. R. Hodgkinson.	F. Dixon.
Bernard Dyer.	A. G. Bloxam.
Edward Barralet.	E. M. Chapman.
Samuel Rideal.	K. J. P. Orton.
T. A. Lawson.	Godfrey Melland.
R. J. Friswell.	T. Slater Price.
H. Silvester.	E. F. Harrison.
T. H. Pope.	J. E. Mackenzie.
Thomas Royle.	J. V. Eyre.
D. A. Sutherland.	F. Southerden.
D. A. Louis.	W. A. Lethbridge.
H. P. Stevens.	G. G. Quinn.
F. J. M. Page.	W. T. B. Ridge.
S. G. Hall.	L. P. Wilson.
Bertram Blount.	H. Wulff Kinnersley.
Charles Watson.	W. A. Handcock.
C. E. Eastick.	A. Marshall.
Peter MacEwan.	W. Rintoul.
J. Lewkowitsch.	J. C. Burnham.
J. Heron.	S. S. Napper.
C. A. Kohn.	W. F. Thomson.
W. F. Reid.	E. W. Lewis.
Oscar Guttman.	W. B. Woodbridge.
S. Dickson.	B. S. Bull.
J. H. Millar.	T. Tickle.
S. Williamson.	W. H. Lewis.
Otto Rosenheim.	James Grant.
P. Schidrowitz.	John Allan.
O. Hohner.	T. R. Duggan.
J. F. Thorpe.	W. C. Reynolds.
J. Hübner.	W. H. Taylor.
L. G. Radcliffe.	H. C. Sayer.

It is proposed—

- (1) On line 7 of By-Law XI. (page 21, fifth line from top), to delete the words "the Council" and insert in their place the words "an Extraordinary General Meeting of the Society";

The part of By-Law XI. would then read:—

"The specific days and hour of meeting to be determined by an Extraordinary General Meeting of the Society."

- (2) To resolve that the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays, at 8 p.m."

The President of the Society has fixed the Extraordinary General Meeting for Thursday, December 12th, at 8 p.m.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 254).

PART II.—THE DETERMINATION OF URANIUM (continued).

Precipitation of Uranium by Ammonium Dihydrogen Phosphate.

As the precipitates formed by disodium hydrogen phosphate were slimy and difficult to wash, it was suggested that possibly this difficulty could be overcome by means of an ammonium phosphate. The precipitant used was ammonium dihydrogen phosphate. The mode of procedure was the same as when disodium hydrogen phosphate was used.

To a solution containing 0.1925 grm. of uranium were added from 0.1 c.c. to 1.5 c.c. nitric acid (sp. gr. 1.42) and sufficient water to make 150 c.c. volume. The solution was brought to boiling, ammonia (sp. gr. 0.90) was added to neutral reaction, and from 1 c.c. to 10 c.c. in excess. The ammonium uranate which formed was taken into solution by the addition of 50 per cent acetic acid, and from 1 c.c. to 5 c.c. in excess. The solutions, then acid with acetic acid, were brought to boiling, and the uranium precipitated by an excess of a saturated solution of ammonium dihydrogen phosphate. The best precipitations, that is, those which were most crystalline and easiest to handle, were formed when about one and a half as much precipitant was added as was necessary for the precipitation. The solutions were boiled for half-an-hour, and the precipitate allowed to settle before filtering. The precipitates were washed three times by decantation, and three times on the filter with a hot dilute solution of ammonium chloride (2 grms. salt to 100 c.c. water). The addition of ammonium chloride or of chloroform to the solution was found unnecessary, as enough ammonium salts were already present. The precipitates which formed were pulverulent and crystalline, and were as readily filtered and washed as the precipitates of ammonium uranate.

The precipitates were dried, separated from the filter-paper, and the paper ignited in a porcelain crucible, after which the precipitate was added, and the ignition continued at "redness" for about five minutes. The crucible was allowed to cool, and the residue moistened with a few drops of nitric acid (sp. gr. 1.42). The mass was dried over a low flame, then re-ignited for from ten to twenty-five minutes at "low redness" over a Bunsen burner. The mass after this treatment, was in all cases a lemon-yellow colour. The crucibles were allowed to cool in a desiccator, and weighed.

The results obtained are given in Table VI.

The filtrates were evaporated and tested for uranium with potassium ferrocyanide. No uranium was indicated.

In several cases when the ignition was done at a temperature above "redness," the precipitate would invariably assume a green colour, especially where the residue was in contact with the crucible. Whenever this occurred, the mass was again moistened with nitric acid (sp. gr. 1.42), dried over a low flame, and re-ignited at "low redness." By this treatment the mass was oxidised to $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

Several precipitates, after having been weighed as uranyl pyrophosphate, were re-ignited over a blast-lamp for about fifteen minutes. The residue, in all cases, after such treatment was entirely green, but when moistened with nitric acid (sp. gr. 1.42), and re-ignited at "low redness," always changed back to lemon-yellow uranyl pyrophosphate, and their weight was the same as the original weight.

Solution No. 15 was allowed to stand for six days before filtering. The appearance of the precipitate was the same as those which were filtered directly.

The weighing of uranium as uranyl ammonium phosphate $(\text{UO}_2\cdot\text{NH}_4\cdot\text{PO}_4)$ was undertaken but without success. The filtering through Gooch crucibles was tried, but owing to the fineness of the precipitate this could not be done. After trying to filter six solutions in this manner, the idea of weighing uranium as uranyl ammonium phosphate was abandoned as impracticable.

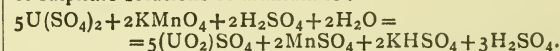
The Volumetric Estimation of Uranium.

Belohoubeck (*Zeit. Anal. Chem.*, 1867, vi., 120; Sutton's "Volumetric Analysis, 1900, p. 375), in 1866, estimated uranium by reducing the solution in a flask with metallic zinc and sulphuric acid. For small amounts of uranium, he states that the reduction is complete in about fifteen minutes, while for larger quantities the time required is much longer. The solutions, after reduction, were diluted and titrated by a standard potassium permanganate solution, the standard of which was made on ferrous ammonium sulphate.

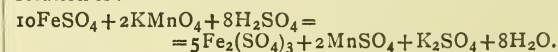
Uranium differs from iron, as regards reduction, in that it is not reduced by hydrogen sulphide. When mercuric salts are present the uranium is, however, reduced by this reagent (Dammer's "Handbuch der Anorg. Chemie," 1893, vol. iii., p. 686).

The permanganate used for titrating uranium solutions is standardised by iron, two atoms of iron corresponding to one of uranium.

The reaction (Mohr's "Lehrbuch der Chem.-Analyt. Titrimethoden," p. 267) which occurs during the titration of sulphate solutions of uranium is:—



The reaction which occurs during the titration of ferrous solution is:—



$5\text{U}(\text{SO}_4)_2$ is equivalent to 10FeSO_4 , or $1\text{U} = 2\text{Fe}$.

The reduction of uranium by zinc and sulphuric acid corresponds to the change of UO_3 to UO_2 (Watts's "Chemical Dictionary," iv., 820).

Experimental.

The fact that iron is so easily, and, at the same time, accurately determined by means of potassium permanganate, and that uranium solutions can be reduced, and then oxidised by potassium permanganate, suggested that possibly, with a few modifications, the Belohoubeck method could be adapted to the technical assay of uranium ores.

In order to demonstrate the best means of reducing uranium solutions, several different reducing agents were employed, the results of which are given below:—

The first series of experiments was made by reducing the uranyl solution by means of zinc and sulphuric acid

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xliii., No. 10.

TABLE VI.—Precipitation of Uranium by Ammonium Dihydrogen Phosphate.

Expt. No.	Approximate dilution.	Salts added.	Temperature of solution after precipitation.	Crucible in which ignited.	Time of ignition. Minutes.	Weight of (UO ₃) ₂ P ₂ O ₇ .	Uranium equivalent.	Theoretical amount of uranium taken.
8.	150	{ NH ₄ NO ₃ NH ₄ C ₂ H ₃ O ₂	{ Boiling-point, boiled for one hour	Porcelain	10	0.2879	0.1924	0.1925
9.	150	"	{ Boiling-point, boiled for ten minutes	"	15	0.2880	0.1924	0.1925
10.	200	"	{ Boiling-point, boiled for three-quarters of an hour	"	20	0.2881	0.1925	0.1925
11.	200	"	" "	"	20	0.2879	0.1924	0.1925
12.	150	{ NH ₄ Cl NH ₄ NO ₃ NH ₄ C ₂ H ₃ O ₂	" "	"	25	0.2881	0.1925	0.1925
13.	150	{ NH ₄ Cl NH ₄ NO ₃ NH ₄ C ₂ H ₃ O ₂	" "	"	25	0.2883	0.1226	0.1925
14.	200	"	" "	"	15	0.2879	0.1924	0.1925
15.	150	{ NH ₄ Cl NH ₄ C ₂ H ₃ O ₂	" "	"	15	0.2878	0.1923	0.1925
16.	150	"	" "	"	15	0.2882	0.1926	0.1925

at boiling temperature, then by means of zinc and hydrochloric acid.

The second series was made by reducing the uranyl solution by means of strips of metallic aluminum, first in dilute sulphuric acid solutions, then in dilute hydrochloric acid solutions.

The third series was made by reducing the uranyl solutions by means of metallic magnesium, first in dilute sulphuric acid, then in dilute hydrochloric acid solutions.

The fourth series was made by passing the uranyl solutions through a long Jones's reductor.

The fifth series was made by reducing the uranyl solution by means of a strong solution of stannous chloride, and destroying the excess of stannous chloride by adding sufficient mercuric chloride, as in the Zimmerman-Reinhart method, so largely used for the estimation of iron.

The standard solution of potassium permanganate was made by dissolving 18.96 grms. of the salt in distilled water, and diluting it to 6 litres, thus making a 0.01 normal solution. The standard was obtained by titrating ferrous sulphate solutions, containing a known quantity of iron. 1 c.c. KMnO₄ = 0.00548 gm. iron.

The uranium standard was calculated from the iron standard by the proportion:—239.6 : 2(55.9) = x : 0.00548; x = 0.01076.

Two equivalents of iron correspond to one equivalent of uranium, or the iron standard multiplied by 2.1425 gives the uranium standard. In order to get the uranium standard in terms of U₃O₈, multiply the iron standard by 2.5243.

The standard of the permanganate solution was verified by taking a measured amount of standard uranium nitrate solution, and reducing it with about 50 grms. of pure zinc and sulphuric acid (30 c.c. sulphuric acid, sp. gr. 1.84, in 150 c.c. of solution). The solution was diluted to 500 c.c., and titrated. The results obtained agreed to the fifth decimal place with those of the iron titration.

(To be continued).

THE ACTION OF SODIUM THIOSULPHATE ON SOLUTIONS OF METALLIC SALTS AT HIGH TEMPERATURES AND PRESSURES.*

By JOHN T. NORTON, Jun.

(Concluded from p. 255).

Experiments with a Salt of Aluminum.

In a series of experiments made according to the method of Chancel, the results of which are shown in Table II.,

the solution in water of a weighed portion of pure ammonium alum was treated with an excess of sodium thiosulphate, and boiled vigorously for periods varying from ten minutes to half-an-hour.

TABLE II.

	Amount of alum taken as Al ₂ O ₃ . Grm.	Amount of Na ₂ S ₂ O ₃ .	Al ₂ O ₃ found.		Error.
			Grm.	Grm.	
1.	0.0537	Large excess	0.0471	0.0066—	
2.	0.0537	" "	0.0397	0.0140—	
3.	0.1083	" "	0.0931	0.0152—	
4.	0.1137	5 grms.	0.0979	0.0158—	
5.	0.1139	2 "	0.1002	0.0137—	

These results substantiate the observations of Gibbs (*loc. cit.*) and of Zimmerman (*loc. cit.*), and show clearly that the boiling of solutions of the aluminum salt and sodium thiosulphate for a reasonable time does not effect the complete precipitation of aluminum as the hydroxide.

Table III. shows the result of submitting solutions of ammonium alum treated with varying quantities of sodium thiosulphate to a pressure of 20 atmospheres in the digester. It usually required about forty minutes to raise the pressure to the limit set; but this limit once reached, the digester was allowed to cool slowly. The duration of an experiment was about two hours.

TABLE III.

Alum taken as Al ₂ O ₃ . Grm.	Amount of Na ₂ S ₂ O ₃ used. Grms.	Al ₂ O ₃ found.		Error.
		Grm.	Grm.	
0.0565	5	0.0633	0.0068+	
0.1132	10	0.1154	0.0022+	
0.1153	5	0.1186	0.0033+	
0.1128	3	0.1129	0.0001+	
0.1126	3	0.1142	0.0016+	
0.1128	2	0.1120	0.0008—	
0.1136	2	0.1121	0.0015—	
0.1128	2.5	0.1136	0.0008+	
0.1124	2.5	0.1127	0.0003+	
0.1134	2.25	0.1133	0.0001—	

This table shows that sodium thiosulphate precipitates aluminum completely as the hydroxide when pressure is employed. The high results seen in some of the experiments appear to be due to the difficulty of removing by ignition the large amounts of sulphur formed in the action, as well as to the salts mechanically included in the precipitate. The amounts of sulphur and contaminating salts present depend upon the amount of thiosulphate taken; therefore, this should be as small as possible, 2 to 3 grms. being sufficient to precipitate all the alumina in

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xii., No. 68.

a grm. of alum. When the amount of thiosulphate is reasonably restricted the weights of alumina accord fairly well with the theory.

Experiments with a Salt of Chromium.

Up to the time of the completion of this work nothing appears to have been done upon the quantitative precipitation of chromium as the hydroxide by means of sodium thiosulphate. Slater (*loc. cit.*) and Rose ("Traité de Chimie Analytique," i., 479) make mention of the action of sodium thiosulphate upon chromic acid, bichromates, and neutral chromates, but give no quantitative data. Recently, however, F. Faktor (*Zeit. Anal. Chem.*, 1900, xxxix., 345) has studied the action of sodium thiosulphate on chromium compounds. This investigator has found that if aqueous solutions of potassium bichromate and sodium thiosulphate are boiled together, a brown precipitate of hydrated Cr_2O_3 , CrO_3 separates out, and the liquid turns yellow owing to the formation of normal chromate. A solution of potassium chromate is unaffected by boiling with thiosulphate, but in presence of ammonium or of magnesium chloride the chromium is separated rapidly and completely in the same form as with the bichromate, and after continued boiling with an excess of thiosulphate all the chromium present is precipitated. Faktor also found that a solution of chromic chloride is completely decomposed by continued boiling with thiosulphate, chromic hydroxide and sulphur being precipitated.

In the experiments shown in Table IV. a weighed quantity of pure potassium bichromate was dissolved in water, a known amount of sodium thiosulphate added, and the whole submitted to a pressure of 20 atmospheres in the digester. After cooling, the precipitate was filtered off on an ashless paper, ignited, and weighed as Cr_2O_3 .

TABLE IV.

	$\text{K}_2\text{Cr}_2\text{O}_7$ taken as Cr_2O_3 .	Amount of $\text{Na}_2\text{S}_2\text{O}_5$.	Cr_2O_3 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0.1330	3.3	0.1341	0.0011+
2.	0.1330	2.5	0.1326	0.0004-
3.	0.1322	2.5	0.1318	0.0004+
4.	0.1303	2	0.1303	0.0000
5.	0.1301	2	0.1310	0.0009+
6.	0.1320	2	0.1322	0.0002+

The results of these experiments are very satisfactory, and show that under pressure sodium thiosulphate precipitates chromium rapidly and completely as the hydroxide. It is advisable to use as small a quantity of thiosulphate as possible in order to prevent the presence of much free sulphur in the precipitate.

Experiments with a Salt of Beryllium.

In experiments dealing with beryllium the salt used was the chloride, a certain amount of which was dissolved in water diluted to a litre, and the amount of beryllium present determined by precipitating with ammonia and weighing as the oxide. Measured quantities of this solution were drawn from a burette as required. When a solution of a salt of beryllium and sodium thiosulphate are merely boiled together, nearly all the beryllium remains in solution. It was expected that the use of pressure would throw out all the beryllium, but, curiously enough, when solutions of beryllium chloride and sodium thiosulphate were submitted in the digester to pressures ranging from 10 to 80 atmospheres, only a partial precipitation of the hydroxide took place.

Experiments with Salts of Zirconium.

To prepare a standard solution of the salt of zirconium it was found to be most convenient to heat the double fluoride of potassium and zirconium with sulphuric acid,

evaporate to dryness in platinum, dissolve the zirconium sulphate remaining in water and enough sulphuric acid to prevent the precipitation of the basic salt, and dilute to standard volume. Measured portions of the solution were taken from a burette as required for the experiments. The presence, however, of so large an amount of sulphuric acid as was necessary to keep the zirconium salt in solution tends to decompose sodium thiosulphate so rapidly that it was found necessary to nearly neutralise the solution with ammonium carbonate before adding the sodium thiosulphate. The solution of zirconium sulphate was standardised by precipitating with ammonia and weighing as the oxide.

In experiment I. of Table V., the solutions of zirconium sulphate and sodium thiosulphate were boiled together for a few minutes and then the precipitate filtered off, ignited, and weighed as the oxide. In experiments 2 to 5 inclusive, similar solutions were submitted to a pressure of 20 atmospheres in the digester.

TABLE V.

	ZrO_2 taken.	$\text{Na}_2\text{S}_2\text{O}_5$ taken.	ZrO_2 found.	Error.
	Grm.	Grms.	Grm.	Grm.
1.	0.0658	3	0.0651	0.0007-
2.	0.0658	3	0.0676	0.0016+
3.	0.0666	2	0.0670	0.0004-
4.	0.0641	2	0.0648	0.0007+
5.	0.0641	2	0.0645	0.0004+

These results clearly show that sodium thiosulphate precipitates zirconium completely as the hydroxide either with or without the aid of pressure.

Experiments with a Salt of Titanium.

The solution of the salt of titanium was obtained by treating the double fluoride of potassium and titanium with sulphuric acid, evaporating to dryness, and dissolving the residue in sulphuric acid and water. The solution was standardised by precipitating the titanium hydroxide with ammonia and then adding an excess of acid as recommended by Gooch (*Am. Chem. Journ.*, vii., 285). This method of procedure avoids the tendency to excessive weight observed when the titanium hydroxide is precipitated by ammonia in presence of salts of the alkalis.

In the following table is shown the effect of treating a solution of titanium sulphate with sodium thiosulphate. Experiment 1 was conducted by merely boiling a solution of the reagents named above, filtering off the precipitate, and weighing as the oxide. In Experiments 2 and 3 the solution of titanium sulphate and sodium thiosulphate was submitted to a pressure of 20 atmospheres in the digester.

TABLE VI.

	TiO_2 taken.	$\text{Na}_2\text{S}_2\text{O}_5$ taken.	TiO_2 found.	Error.
	Grm.	Grms.	Grm.	Grm.
1.	0.0240	2	0.0237	0.0003-
2.	0.0240	2	0.0240	0.0000±
3.	0.0240	2	0.0240	0.0000±

These results show that titanium is completely precipitated by sodium thiosulphate either with or without the aid of pressure.

To recapitulate, I have shown that sodium thiosulphate will completely precipitate aluminum, chromium, zirconium, and titanium as the hydroxides with the aid of high temperature and pressure. Beryllium is only partially precipitated under similar conditions. Mere boiling for a reasonable time will not precipitate aluminum and chromium, but it is sufficient in the case of zirconium and titanium.

In conclusion, I wish to thank Prof. F. A. Gooch for his kind advice and assistance.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation and published, or passed for publication, in the *Transactions* :—

129. "Additional Notes on Dinitro-orthoanisidine. A Chemical Reaction in which one of the Products contains the same Reaction." By R. MELDOLA and J. V. EYRE.

The authors give further evidence in support of the constitutional formula assigned to the dinitroanisidine already described (*Proc.*, 1901, xvii., 131). The 3:4:6-triaminoanisole and the corresponding 3:4-diamino-6-acetaminoanisole both form azines on condensation with benzil, which are described. The view put forward (*loc. cit.*), that the eliminated nitro-group comes out in the form of nitrous acid, is confirmed by quantitative determinations of the amount of diazo-oxide formed from known weights of dinitroanisidine in acetic acid solution with accurately titrated solutions of nitrite. The latter was added to the extent of one-fourth of the theoretical quantity required on the assumption that one molecule of dinitroanisidine requires one molecule of nitrite. In all cases the diazo-oxide produced, as determined by the quantity of azo- β -naphthol compound formed, was far in excess of that capable of being produced by the nitrite added, thus proving that the nitro-group eliminated by the nitrous acid continues the process of diazotisation.

130. "Ethyl Sec-octyl Tartrate and its Dibenzoyl and Diacetyl Derivatives." By J. McCRAE.

Diethyl tartrate and octyl alcohol when saturated in the cold with hydrochloric acid give ethyl octyl tartrate, which is purified by distillation and washing with water. By the action of excess of acid chloride on this mixed ester, the dibenzoyl and diacetyl derivatives have been prepared. The optical rotation of these compounds has been determined, and the author finds that the molecular rotations are similar to the constants for the corresponding diethyl tartrates. This is a confirmation of the rule suggested by Guye, namely, that when substitution is effected at a point sufficiently far removed from the asymmetric carbon atom, only a slight change in the rotation is produced.

131. "The Esterification of 3-Nitrophthalic Acid." By A. MCKENZIE.

The esterification of 3-nitrophthalic acid does not proceed normally in accordance with V. Meyer's rule. The author has studied the action of amyl and methyl alcohols on 3-nitrophthalic acid and its anhydride, and shows that the isomeric α - and β -acid esters are formed on esterification, as well as the neutral ester in certain cases.

The compounds, 2-isoamyl-3-nitrophthalic acid and d-2-amyl-3-nitrophthalic acid are also described.

132. "Derivatives of 3-Nitrotolyl-4-Hydrazine." By F. G. POPE and J. M. HIRD.

The hydrochloride was prepared by Meyer and Lecco's method, and forms orange-red plates or needles, m. p. 190—191° with decomposition. The free base forms red tufts of needles, m. p. 110°. The pyruvic acid hydrazone forms yellow needles, m. p. 203° with decomposition. The ethyl ester of the pyruvic hydrazone is obtained as small, yellow needles, m. p. 140°. The semicarbazide forms small, yellow needles, m. p. 201°, and gives a deep violet colouration with cold alcoholic potash. The following compounds have also been prepared:—Salicylaldehyde hydrazone, scarlet needles, m. p. 226°; furfuraldehyde hydrazone, red needles, m. p. 165—166°; benzaldehyde hydrazone, red needles, m. p. 166°; phenylthiosemicarbazide, tufts of golden-yellow needles, m. p. 188°; allylthiosemicarbazide, yellow needles, m. p. 168—170°; acetyl-nitrotolyl hydrazone, yellow needles, m. p. 161°.

133. "The Constituents of the Sandarac Resins." By T. A. HENRY, D.Sc.

The sandarac of commerce is the naturally exuded resin

of various species of *Callitris*, usually either *C. quadri-valvis* or *C. verrucosa*.

Both varieties of resin consist of a mixture of resin acids and terpenes separable by steam distillation. From the latter, d-pinene has been isolated and identified. The chief volatile constituent is a diterpene, boiling at 265°, $\mu_D = 1.5215$, $[\alpha]_D = +55^\circ$, which behaves like a saturated substance, forming no additive compounds with bromine, hydrogen chloride, or nitrosyl chloride. Two resin acids have been isolated and examined. One of these has the composition $C_{20}H_{30}O_2$ (m. p. = 171°, b. p. 265°, 11 m.m.), and closely resembles in behaviour the isomeric d pimaric acid of Vesterberg (*Ber.*, 1885, xviii., 3331), but is optically inactive, and is therefore named inactive pimaric acid. On reduction with hydriodic acid, it gives a diterpene, $C_{20}H_{32}$. On oxidation with permanganate, pimaric acid yields acetic acid, and a crystalline substance melting at 206°, which is probably trimellitic acid.

The second resin of sandarac has not been obtained in a crystalline form, but the highly deliquescent sodium salt and the characteristic lactone have been prepared; from analyses of these, the formula of the free acid is probably $C_{30}H_{48}O_5$. For this substance, the name callitricolic acid has been retained. The acid is remarkably resistant to the action of reagents, being unattacked even by hot fuming nitric acid. When heated in a vacuum, it is decomposed with the formation of carbon dioxide, and a diterpene identical with that occurring naturally in the resin.

134. "Condensation of Phenols with Esters of the Acetylene Series." Part VI. By S. RUHEMANN and E. WRAGG, B.A.

The authors have continued the research on the interaction of phenols with ethyl chlorofumarate and ethyl phenylpropionate, using eugenol and m-xyleneol. From the former phenol they obtained ethyl eugenoxym-fumarate and the corresponding acid, from which they have not been able to prepare the pyrone-compound in a pure state. m-Xyleneol reacts with ethyl chlorofumarate to form ethyl-m-xyleneoxym-fumarate, the acid of which, on treatment with concentrated sulphuric acid, yields 6:8-dimethyl-1:4-benzopyrone 2-carboxylic acid (m. p. 210° with decomposition). This, on heating, loses carbon dioxide, giving 6:8-dimethyl-1:4-benzopyrone (m. p. 80—81°). With ethyl phenylpropionate m-xyleneol forms ethyl β -m-xyleneoxycinnamate, which is hydrolysed by alcoholic potash to the acid. This yields, on heating, m-xyleneoxystyrene, and is decomposed by sulphuric acid into carbon dioxide acetophenone, and m-xyleneol.

The authors have attempted to ascertain whether only the phenyl group in the aryl ethers of the unsaturated hydroxy-acid prevents the condensation to the pyrone compound taking place, and have found that β -phenoxy-crotonic acid, $CH_3C(O \cdot C_6H_5) \cdot CH \cdot CO_2H$, on heating, loses carbon dioxide, and yields β -phenoxypropylene, $CH_3C(O \cdot C_6H_5) \cdot CH_2$ (b. p. 170°), and with sulphuric acid it breaks up into carbon dioxide, acetone, and phenol. To determine whether the condensation to the 1:4-benzopyrone compound depends upon the configuration of the aryl ethers of the hydroxy-acid, the authors have treated ethyl β -isochlorocrotonate instead of its stereoisomeride with sodium phenolate; they find, however, that the same substance is formed as when ethyl β -chlorocrotonate is used.

135. "The Hydrobromides of Undecylenic Acid." By J. WALKER and J. S. LUMSDEN.

When hydrobromic acid is added to undecylenic acid, a bromo-undecylic acid, m. p. 51°, is formed at the same time as Brunner's acid, m. p. 35°. It is shown that the former is ω -bromo-undecylic acid, $CH_2Br(CH_2)_9CO_2H$, and not Brunner's acid as was previously supposed.

136. "Normal Decane-dicarboxylic Acid." By J. WALKER and J. S. LUMSDEN.

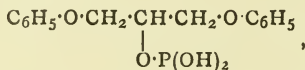
This acid was prepared by electrosynthesis from pimelic acid and was found to be identical with an acid prepared from ω -bromo-undecylic acid. The solubility in water

differs entirely from the solubility of the acids described by Nördlinger and Komppa.

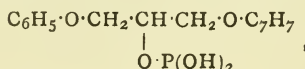
137. "Action of the Chlorides of Phosphorus on certain Aromatic Ethers of Glycerin." By D. R. BOYD.

The author has studied the behaviour of symmetrical diphenyl glycerol-ether and some similar compounds when treated with the pentachloride and trichloride of phosphorus respectively.

Phosphorus pentachloride with diphenyl-glycerol-ether yields β -chloro-trimethylene-glycol-diphenyl-ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot O \cdot C_6H_5$, m. p. 37° . Phosphorus trichloride and diphenyl-glycerol-ether give a product which, on treatment with water, yields glyceryl-diphenyl-ether-phosphorous acid,—



m. p. $119-120^\circ$. Phenyl- β -tolyl-glycerol-ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot O \cdot C_7H_7$, m. p. $73.5-76^\circ$, which is obtained by the action of phenyl-glycid ether on β -cresol, yields β -chloro-trimethylene-glycol-phenyl- β -tolyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot O \cdot C_7H_7$, m. p. 60° , and glyceryl phenyl- β -tolyl-ether phosphorous acid,—



m. p. $106-107^\circ$.

Further, di- β -tolyl-glycerol-ether yields β -chloro-trimethylene-glycol-di- β -tolyl ether,—



m. p. 70° , and glyceryl di- β -tolyl-ether-phosphorous acid, m. p. $111-112^\circ$.

138. "The Autofermentation and Liquefaction of Pressed Yeast." By A. HARDEN and S. ROWLAND.

The time required for the liquefaction of pressed yeast is greatly diminished by rise of temperature, whilst the rate of evolution of carbon dioxide is greatly increased. The evolution of gas ceases as soon as the yeast becomes liquid, and hence is small at 50° , owing to the rapid liquefaction of the mass (one to one and a-half hours), whilst the total volumes evolved at 39° and 26° do not differ greatly although the times required for liquefaction are five and fifty-three hours respectively. At 14° the time required is sixteen days, the rate of evolution being extremely slow, and the total volume evolved about 75 per cent of that produced at 26° . Alcohol is produced simultaneously, the process being apparently a true alcoholic fermentation of the glycogen of the cell. Microscopic examination shows that as the evolution of gas proceeds the glycogen disappears, and the vacuole of the cell increases in size. Finally, the vacuolar contents are discharged, and the cell appears shrunken and irregular in outline, whilst the protoplasmic contents are highly granular.

In the presence of oxygen, a process of oxidation accompanies the evolution of carbon dioxide, a considerable rise of temperature being produced, and the total volume of carbon dioxide increased. When exposed to a continuous current of oxygen, a sample of yeast was found to lose 26 per cent of its carbon.

139. "Non-existence of the So-called Suboxide of Phosphorus." Part II. By C. H. BURGESS and D. L. CHAPMAN.

Substances obtained according to the methods described by Michaelis and Pitsch (*Ann.*, 1899, cccx., 45) and Michaelis and v. Arend (*Ann.*, 1901, cccxiv., 259) have been prepared and analysed, and shown to contain such a large amount of hydrogen that they cannot be regarded as a suboxide, but as red phosphorus containing hydrogen compounds. The authors show that some of the analytical results of Michaelis and Pitsch indicate that the substances prepared by them contained water, and that the

proof of the absence of hydrogen in the substance, described by them as a pure suboxide, is inconclusive.

As red phosphorus is easily soluble in aqueous alcoholic potash, with formation of a red solution, red phosphorus resembles in this respect the so-called sub-oxide.

The authors conclude that both the properties and the analytical results support the view that the substances hitherto described as sub-oxides of phosphorus are only impure forms of amorphous phosphorus.

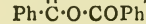
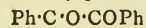
140. "The Action of Ammonia on Metals at High Temperatures." By G. T. BEILBY and G. G. HENDERSON.

Platinum, gold, silver, copper, iron, nickel, and cobalt have been exposed to the action of ammonia at temperatures ranging from 400° to 900° . In every case the physical effect of the treatment was to disintegrate the metal completely, whilst a large proportion of the ammonia was resolved into its elements. The fracture of metals which have been exposed to this action is spongy or cellular; under the microscope the metal appears as if it had been suddenly cooled whilst in a state of active effervescence. The penetration of the ammonia molecules into the metal is remarkably quick if the conditions are favourable.

The authors believe that the physical effects which result from the action of ammonia upon metals at high temperatures are due to the alternate formation and dissociation of nitrides taking place between certain narrow limits of temperature, the reaction going in one direction or the other according as ammonia or hydrogen molecules preponderate in the gases which are in contact with the molecules of the metal at and below the surface. In several cases the formation of nitrides has been definitely proved. The absorption of small quantities of nitrogen by pure iron renders it hard and brittle like steel.

141. "The Condensation of Benzil with Dibenzyl Ketone." By G. G. HENDERSON and R. H. CORSTORPHINE, B.Sc.

Benzyl and dibenzyl ketone readily condense when warmed with excess of aqueous potash, and tetraphenylcyclopentenolone is produced. It melts at 208° , is readily soluble in benzene but only sparingly so in alcohol. It yields an *oxime*, m. p. 167° , which when heated in alcoholic solution with β -bromophenylhydrazine gives a crystalline *hydrazone* melting at 169° . The *acetyl* derivative melts at 218° . Tetraphenylcyclopentenolone quickly reduces potassium permanganate, does not combine with bromine, but is slowly converted into a very unstable *bromine* derivative. When cautiously oxidised in the cold with chromic anhydride dissolved in glacial acetic acid, tetraphenylcyclopentenolone gives benzoic acid and a neutral compound, $C_{28}H_{20}O_4$, possibly *isobenzil*,—

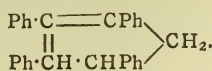


colourless crystals, m. p. $164-165^\circ$.

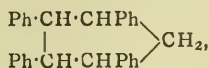
Tetraphenylcyclopentenolone undergoes partial reduction when boiled for an hour or two under a reflux condenser with hydriodic acid and red phosphorus, but the product is not tetraphenylcyclopentenone, but a *tetra-phenylcyclopentenol*, which crystallises in colourless needles, m. p. 162° , is readily soluble in benzene, very sparingly so in alcohol; it quickly decolorises potassium permanganate in alkaline solution. It does not react either with hydroxylamine or with phenylhydrazine, but gives an *acetyl* derivative, colourless tablets, m. p. 181° . Bromine converts it into a *bromine* derivative, $C_{29}H_{22}BrOH$, colourless needles, m. p. 215° . By treatment with phosphorus pentachloride or alcoholic hydrogen chloride it yields a *mono-chlorotetraphenylcyclopentene*, $C_{29}H_{23}Cl$, colourless prisms, m. p. 181° .

When heated at 180° in a sealed tube with hydriodic acid and red phosphorus, tetraphenylcyclopentenol is reduced to two hydrocarbons, $C_{29}H_{24}$ and $C_{29}H_{26}$, which can be separated by means of ether, in which the former

is easily and the latter somewhat sparingly soluble. From its mode of formation the former is no doubt 1 : 2 : 4 : 5-tetraphenylcyclopentene,—



The other hydrocarbon is obtained in colourless crystals from alcohol. It melts at 80°–81°, and is apparently identical with the 1 : 2 : 4 : 5-tetraphenylcyclopentane,—



already prepared by Wislicenus in a different manner. The former melts with decomposition at over 300°, and the latter at 80°–81°.

142. "The Chlorodibromo- and Dichlorobromo-benzenes." By W. H. HURTLEY, D.Sc.

Twelve tri-substituted chlorobromobenzenes should exist according to theory. The two symmetric compounds have been obtained by Hantzsch, Schleissing, and Jäger (*Ber.*, 1897, xxx., 2334), the 1-chloro-3 : 5-dibromobenzene from 3 : 5-dibromoaniline. The author has prepared all the twelve compounds from anilines of known constitution, many of which have not previously been obtained. The asymmetric compounds were prepared from dihalogen anilines, by replacing the amino-group by chlorine or bromine by Gattermann's method (*Ber.*, 1890, xxiii., 1222), and by eliminating the amino-group from asymmetric trihalogen anilines. The symmetric compounds resulted from the symmetric trihalogen anilines by eliminating the amino-group. The vicinal compounds were obtained from vicinal trihalogen anilines, also by eliminating the amino-group.

All the trichlorobromobenzenes are solids; the vicinal crystallise in well-defined rhombic plates; the symmetric, in long slender prisms; and the asymmetric in short thin prisms. All are very soluble in benzene, ether, chloroform, and petroleum, but less so in alcohol, from which they can be readily crystallised. The vicinal and symmetric compounds are easily volatile in steam, whilst the asymmetric are less so.

Asymmetric.—1 : 2-dichloro-4-bromobenzene, prisms, m. p. 24°5', b. p. 237°; 1 : 3-dichloro-4-bromobenzene, prisms, m. p. 25°, b. p. 235°; 1 : 4-dichloro-2-bromobenzene, prisms, m. p. 33°, b. p. 235°; 1-chloro-3 : 4-dibromobenzene, prisms, m. p. 35°5', b. p. 256°; 1-chloro-2 : 4-dibromobenzene, prisms, m. p. 27°, b. p. 258°; 1-chloro-2 : 5-dibromobenzene, prisms, m. p. 40°5', b. p. 259°.

Symmetric.—1 : 3-dichloro-5-bromobenzene, slender prisms, m. p. 77°5', b. p. 232°; 1-chloro-3 : 5-dibromobenzene, slender prisms, m. p. 99°5', b. p. 256°.

Vicinal.—1 : 2-Dichloro-3-bromobenzene, rhombic plates, m. p. 60°, b. p. 243°; 1 : 3-dichloro-2-bromobenzene, rhombic plates, m. p. 65°, b. p. 242°; 1-chloro-2 : 6-dibromobenzene, rhombic plates, m. p. 69°5', b. p. 265°; 1-chloro-2 : 3-dibromobenzene, rhombic plates, m. p. 73°5', b. p. 264°.

The following new anilines and anilides were also obtained:—3 : 6-Dichloro 4-bromoaniline, needles, m. p. 91°, and its acetyl derivative, prisms, m. p. 189°; 2 : 3-dichloro-4-bromoaniline, needles, m. p. 77°5', and its acetyl derivative, prisms, m. p. 138°5'; 2 : 4-dichloro-5-bromoaniline, flattened prisms, m. p. 86°, and its acetyl derivative, prisms, m. p. 192°; 2 : 4-dichloro-3-bromoaniline, plates, m. p. 78°, and its acetyl derivative, prisms, m. p. 138°; 3 : 5-dichloro-4-bromoaniline, needles, m. p. 129°, and its acetyl derivative, short prisms, m. p. 220°; 3-chloro-4 : 6-dibromoacetanilide, prisms, m. p. 174°; 3-chloro-2 : 4-dibromoaniline, plates, m. p. 88°, and its acetyl derivative, prisms, m. p. 152°; 2-chloro-4 : 5-dibromoaniline, flattened needles, m. p. 93°, and its acetyl derivative, needles, m. p. 193°; 2-chloro-3 : 4-dibromoaniline, plates, m. p. 91°, and its acetyl derivative, needles, m. p. 146°.

Extra Meeting, October 31st, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

DR. ARMSTRONG delivered the

FRANKLAND MEMORIAL LECTURE.

Frankland was born at Churchtown, Lancashire, in January, 1825. When about seven years old he went with his mother and stepfather to Lancaster, where he lived until he entered Playfair's laboratory in 1840; he there attended a private school kept by a Mr. Willasey, until he was twelve years old, when he entered the Lancaster Grammar School in the lowest class, leaving it at the age of fifteen from the highest. His mother appears to have had a great influence in developing his scientific tastes, leading him as a child to pay attention to surrounding objects; these lessons were the means of causing him to seek information about natural phenomena for himself in books. Before he was twelve, he had read many books on chemistry, electricity, and magnetism, among others Priestley's *Researches on Electricity*. He thus learnt how to make a Volta's pile, with which he decomposed water; and having obtained a magnet, made most of the experiments of which he had read. His master appears to have encouraged him—for on hearing that he was showing experiments to his school-fellows, he invited him to bring his apparatus into the class room and demonstrate to the school. When about twelve years old he had a strong inclination for a mechanical trade, and having access to a cabinet-maker's workshop, acquired no slight skill. Mr. Willasey, however, dissuaded him, and awakened his ambition by telling him that he ought to aim at becoming a doctor; but as his parents were led to suppose that to give him a medical training was beyond their means, on leaving school he was apprenticed to a druggist in Lancaster. The six years he spent in this capacity were years of the hardest labour. His master not only never attempted to teach him anything, but did his best to hinder his scientific advance. But Frankland's ardour was not to be damped; by rising at four, he managed to get one hour and a-half for botanical work before the day's toil began. During the three years he was at the Lancaster Grammar School, he was able to carry on chemical experiments in a laboratory fitted up in the house of a school-friend; and as an apprentice he enjoyed the friendship of two men—Mr. Christopher Johnson, M.R.C.S., and Dr. James Johnson, who advised him what to read, and lent him apparatus, the latter even fitting up a laboratory in which Frankland and other druggists' apprentices in the town spent their evenings, Mr. Johnson occasionally telling them of Dalton's work, which was then going on.

It was on Mr. Johnson's advice that Frankland entered Playfair's laboratory in 1845. Playfair had then just been appointed organic chemist to the Government Department of Woods and Forests, of which the Geological Survey was a branch. Before six months had passed, Playfair made him his assistant at the College for Engineers, Putney; later on, early in 1847, he became Playfair's chief assistant. Meanwhile he had been offered the post of Professor of Chemistry in the Royal Agricultural College, Cirencester, and had decided to accept the office; but a difficulty arising, and acting on the advice of Kolbe, then one of Playfair's assistants, he decided instead to go to Germany. Kolbe and he went together to Marburg in May, 1847. In the autumn he returned to England to take up the position of lecturer on botany, chemistry, and geology at Queenwood College, Hants. There he met Tyndall, and so great was the ardour of the two young men that they rose at four and taught each other until eight o'clock before doing their work in the school. He returned to Germany again to work with Bunsen, in October, 1848, Tyndall, who at that time thought of becoming a chemist, accompanying him. He

took the degree of Ph.D in June, 1849, and shortly afterwards became engaged to Fräulein Fick, whom he married in 1851. In August, 1849, he went to Giessen to work in Liebig's laboratory. At Christmas he left for Berlin, intending to work with Rose, but receiving there the offer of the chair vacated by Playfair at the Putney College, he returned home. He remained at Putney until January, 1851, when he became Professor of Chemistry at Owens College, Manchester. In October, 1857, he returned to London as lecturer on chemistry in St. Bartholomew's Hospital. In 1863, he resigned this post to become Professor of Chemistry in the Royal Institution. In 1865, he succeeded Hofmann at the Royal College of Chemistry and Royal School of Mines, a post which he held until he retired in 1885. Meanwhile, in 1868, he had been appointed a member of the Rivers Pollution Commission. He died on August 9, 1899.

Frankland began research work with Kolbe very few months after entering Playfair's laboratory; before they left for Germany—within eighteen months of his having commenced to study chemistry systematically—they had completed their work on the hydrolysis of the nitriles, which led to the determination of the constitution of the great group of acids now known as carboxylic acids. They had begun to study the action of potassium on ethyl cyanide with a view to isolating ethyl; this work was completed in Marburg, and Frankland made his maiden appearance as reader of a paper before the Chemical Society in communicating the results which Kolbe and he had obtained. As soon as he was installed at Queenwood, he began independent work, and sought to isolate the alcohol radicles. On continuing this research, on the occasion of his second visit to Bunsen's laboratory, he soon succeeded in preparing "ethyl" and "methyl," and in the course of these experiments made the all-important discovery of zinc methyl and ethyl. The amyl compounds were studied in Liebig's laboratory. At Putney he continued his work on organo-metallic compounds; and it was here that he studied the action of chlorine on stannethyl, &c., and was first led to discover the law of valency; this work was completed at Manchester; the memoir in which Frankland formulated the doctrine which must hereafter always be associated with his name was read to the Royal Society on June 17, 1852.

Besides giving an account of Frankland's early education and subsequent career, and considering his character, Dr. Armstrong entered somewhat fully into an analysis of the work he did with Kolbe; he then proceeded to consider his investigations relating to the isolation of the hydrocarbon radicles, and his researches on the organo-metallic compounds, which culminated in the discovery of the doctrine of valency, leaving the vast mass of work—chemical and physical—which he did subsequently to be dealt with in the printed memoir. Attention was called to the great importance of Frankland and Kolbe's work on the acids of the acetic series. The two papers in which their results are described were referred to as deserving to rank as classics, as specimens of highly original and clearly reasoned precise argument, as well as on account of the importance of the results they disclosed. That they were in no way appreciated at the time of publication was due to the extraordinary hold which Gerhardt's type-system had obtained. For a like reason, Frankland's statement of the doctrine of valency produced originally but a slight impression, and it was only at a later stage—owing to the use that Kekulé had made of it in discussing the constitution of carbon compounds, benzene especially—that its importance became recognised, and it became the guiding principle; and even then Frankland's services were to a great extent overlooked. It was beyond the power of his contemporaries, in fact, to appreciate the bearings of his discoveries when they were first made known; and when the wave of Gerhardtism had spent its force, they appeared almost commonplace, so great had been the advance in knowledge meanwhile, and so insensibly had Frankland's ideas crept into their minds.

Reasons were fully stated which appear to justify the belief that Kekulé must have derived his inspiration from Frankland, who alone is to be regarded as the discoverer of the doctrine of valency—Kekulé's great work having been to develop the consequences of its application to carbon compounds.

Taking the whole of Frankland's work into account, it constitutes a record which is altogether remarkable as evidence of his originality, of the catholic character of his interests, of his practical ability, and of his vigour; it must serve to place him in the very highest rank among the chemists of the century, whilst his early work entitles him to be regarded as one of the great pioneers in establishing the modern doctrine of constitution.

On the motion of Professor ODLING, seconded by Sir H. E. ROSCOE, a vote of thanks was passed to Dr. Armstrong for his lecture.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22nd, 1901.

Prof. S. P. THOMPSON, President, in the Chair.

PROF. W. CASSIE read a paper on "*Multiple Transmission Fixed Arm Spectroscopes.*"

The simplest form of spectroscope shown consisted of two half prisms, silvered on the back, between which a beam of light goes backwards and forwards with a slight upward inclination. The result in dispersing and resolving power is equivalent to direct transmission through a long train of prisms. The collimator and observing telescope are fixed, and adjustment is made by a double tangent screw which moves both the prisms. Two other types constructed on a similar principle were described, of which one had one prism and two speculum mirrors, and the other had two refracting prisms and a reflecting right angled prism. The adjustments of these instruments are simple, and their power great. By a small movement of an adjusting screw the observer can produce great changes of dispersion by passing from one to another of the series of spectra which are produced.

Prof. J. PERRY asked if the third form of spectroscope, in which there is total internal reflection, had been tried experimentally. The amount of light lost at total internal reflection is much less than at reflection from mirrors, and he had found that the chief difficulty in using multiple reflections from mirrors was the great absorption of light.

Mr. T. H. BLAKESLEY asked if there was any confusion due to overlapping of the spectra.

Mr. R. T. GLAZEBROOK said he would like to know whether the author had any measure of the relative brightness of the first and last spectra.

Mr. W. F. STANLEY said that by using three prisms instead of two it would be possible to substitute, in the first form of spectroscope, total internal reflection for normal reflection at a silvered surface.

The CHAIRMAN suggested a possible way of improving the third arrangement by using two prisms with their apices outwards, refracting at both foci, but not in the position of minimum deviation. Twenty-five years ago the present Astronomer Royal suggested the use of half-prism spectroscopes, and although they are often described in books they are seldom actually used. The advantage of using total internal reflection is well known, and is exemplified in binoculars, in some of which there are eight reflections from the object-glass to the eye-piece. He congratulated the author upon the mechanical arrangements used in his spectroscopes.

Prof. CASSIE said that there was no confusion of spectra due to overlapping. With an ordinary Bunsen burner sodium flame a series of about five spectra are easily observed with dispersion equivalent to direct transmission through ten full-sized prisms. The loss of light at the reflections limits the number of transmissions that can be

used; but he believed that no other spectroscope with only two prisms would give dispersing power and resolving power in any way approaching the instrument described.

Prof. W. CASSIE then read a paper on "*The Measurement of Young's Modulus.*"

The apparatus described consisted of a horizontal needle (a bar of large moment of inertia), supported by a bifilar suspension made of the wire of which the stretch modulus is to be measured. The periods of the pitching, rolling, and bifilar oscillations of this system are observed, and an expression for the stretch modulus is obtained, which involves no measurements except the weight of the needle and the periods of the oscillations. The necessary adjustments, and the means of eliminating residual errors of adjustment, were described for two forms of the apparatus. One form also affords a simple means of statical measurement, by hanging a small weight on the needle at measured distances from the centre, calculating the difference of tension produced in the wires, and observing with a mirror and scale the consequent dip of the needle.

Dr. CHREE said that it would be possible to get a check on the theory by placing the movable weights at various positions on the needle, and observing the times of swing for pitching and bifilar vibrations. The ratio of the squares of these times should remain constant. It is difficult to say exactly what the apparatus measures, and he would like to see numerical results before expressing an opinion upon it.

Prof. J. PERRY said it would have been interesting to have had results from the apparatus so that they could be compared with those obtained by other methods. In the bifilar vibration there is a small twist in the wires, on account of which the torsional rigidity of the material affects the time of swing. He drew attention to the necessity of having the tensions in the two wires equal.

Mr. R. T. GLAZEBROOK, referring to the arrangement for clamping the bifilar at the top, pointed out that a small slip would modify the whole of the theory. An advantage of the apparatus lay in the fact that the wires used were shorter than those necessary in other methods. It was an interesting and ingenious application of theory to the methods of measuring Young's modulus.

Mr. WHIPPLE asked how the rolling and bifilar vibrations were experimentally separated.

Mr. A. CAMPBELL suggested that the difficulty of equality of tensions in the wires could be reduced by using longer wires a greater distance apart.

Prof. H. L. CALLENDAR said he had found that the torsional effect in a bifilar vibration was negligible, and that the flexure effect was not important. The absolute rigidity of the fastening at the top was the greatest difficulty.

Prof. CASSIE said his object had been rather to describe and exhibit the apparatus than give numerical results, although he had obtained numbers agreeing with those got by other methods. The mirrors for observing the vibrations were so placed upon the apparatus that each one was affected only by the particular vibration which it was designed to measure.

A paper entitled "*Notes on Gas-Thermometry*" (Part II.), by Dr. P. CHAPPUIS, was read by Dr. HARKER.

Messrs. Holborn and Day have published recently in a research on the air thermometer the results of a new determination of the expansion of Berlin porcelain between 0° and 1000° . The author has already drawn attention in a former note to the fact that part of the divergence found between the results of Callendar and Griffiths, and of Harker and himself, for the boiling-point of sulphur may be attributed to the uncertainty in the values assumed for the expansion of porcelain. In the present paper the author examines the way in which their results would be modified by the introduction of the dilatation deduced from the experiments of Messrs. Holborn and Day. It follows from the introduction of the new values that the boiling-

point of sulphur deduced from experiments with a porcelain reservoir thermometer would be lowered from $445^{\circ}2'$ to $444^{\circ}7'$, a number very close to that obtained by Callendar and Griffiths. In a second part of the paper Dr. Chappuis has re-calculated the divergences between the uncorrected nitrogen scale and the theoretical scale, and finds that the difference between these values and those given previously is too small to be of any practical importance.

The SECRETARY read a letter from Mr. A. E. TUTTON, in which he said that he was working at the expansion of porcelain, and hoped to present a communication to the Society shortly.

Prof. H. L. CALLENDAR said that he was highly gratified to see that the application of the correction for the expansion of the bulb of Dr. Chappuis's gas-thermometer, deduced from Holborn and Day's results, gave a value, $444^{\circ}7'$, for the boiling-point of sulphur in such close agreement with the value $444^{\circ}5'$ deduced by Mr. Griffiths and himself in 1890. The agreement was really much closer than appeared at first sight, because the remaining difference of two-tenths of a degree in the results was almost exactly accounted for by the scale difference of the constant pressure and constant volume thermometers, according to the theory of Joule and Thomson. It was also interesting to remark that the corrected result found by Dr. Chappuis was in very close agreement with that deduced from their own observations by Messrs. Holborn and Day. Dr. Chappuis had not referred in the present note to the work of Bedford on the expansion of Bayeux porcelain, which he had criticised in a previous paper. A comparison of results would show that Bedford's results agreed very fairly, allowing for the difference of material, with Holborn and Day's, from 200° to 600° C.; and that both differed from those of Dr. Chappuis between 0° and 80° , when extrapolated, in a precisely similar manner. It was quite possible, as he (Prof. Callendar) had previously suggested, that the expansion of porcelain between 0° and 100° was anomalous. It appeared certain that some anomaly in the expansion at 800° was indicated both in the experiments of Bedford and also in those of Holborn and Day. It was also clear that Dr. Chappuis's results for Bayeux porcelain when extrapolated would agree with Bedford's at a temperature a little above 100° C., or very nearly at the same point at which his results for Berlin porcelain agreed with those of Holborn and Day.

Mr. R. T. GLAZEBROOK said he had felt for some time that it was of importance that the difference between the results of Callendar and Griffiths, and of Chappuis and Harker should be explained, and he was glad that the agreement was now so satisfactory.

The Society then adjourned until December 13th.

NOTICES OF BOOKS.

Blowpipe Analysis. By J. LANDAUER, Member of the Imperial Germany Academy of Naturalists. Authorised English Edition, by JAMES TAYLOR, B.Sc., A.R.S.M. London: Macmillan and Co. New York: The Macmillan Company. 1901.

THE third edition of this well-known text-book is not merely a reprint of that issued in 1892, but it brings the work quite up to date.

An interesting historical sketch of blowpipe analysis is given, taking the subject back to the year 1660, but its first actual application to chemical research appears to have been by Kunkel in 1679. Johann Gottlieb Gahn, 1745—1818, was so skilled in its use that he could show the metallic copper from the ash of a quarter sheet of paper; and Berzelius, Plattner, Bunsen, Faraday, and Wollaston have all contributed to the progress of blowpipe analysis.

Many alterations have been made, and a good deal of new matter has been added to the text.

We notice a considerable extension of the details of flame colouration tests, and the use of the spectroscope; *wave-lengths* are given of the standard lines instead of the old meaningless scale divisions.

Tables of elements and atomic weights are given, but we are sorry to see they are faulty; didymium is included instead of neodymium and praseodymium.

The size and appearance of the book remain as before, and it is well indexed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

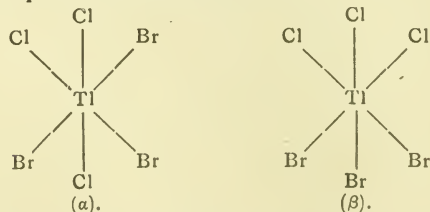
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxi., No. 19, November 4, 1901.

Chemical Effects produced by the Rays emitted by Radium.—Henri Becquerel.—Radiation from radium is composed of—(1) A portion deviable by the magnetic or electric field and identical with cathode rays; (2) a non-deviable portion, of which a fraction is very absorbable and the other portion exceedingly penetrating, thereby partially escaping measurement, owing to the difficulty of stopping it and transforming it into absorbable energy. The author examines the various chemical changes which occur, due to these portions, separately. M. and Mme. Curie have already noticed the coloration effects produced on glass, porcelain, and paper. Amongst exothermic phenomena, the author now examines the transformation of white into red phosphorus under the influence of radium rays. A perceptible change takes place in twenty-four hours. Another action examined is the reduction of mercury bichloride in presence of oxalic acid. A precipitation of calomel is produced under the action of radium rays. Further experiments are described which were performed on germinating seeds under the action of radium.

Decomposition of Calcium-ammonium and of Lithium-ammonium by Ammonium Chloride.—Henri Moissan.—The discovery of the solubility of ammonium salts in ammonia led the author to undertake some new experiments with the liquefied gas. Calcium-ammonium, $\text{Ca}(\text{NH}_3)_4$, and lithium-ammonium, $\text{Li}(\text{NH}_3)$, were allowed to react on a solution of ammonium chloride in liquid ammonia at a temperature of -80° . Under these conditions, ammonia, hydrogen, and the group NH_4 are set free, ammonium not being isolated. The reactions are represented by the following equations:— $2\text{NH}_4\text{Cl} + \text{Ca}(\text{NH}_3)_4 = \text{CaCl}_2 + 4\text{NH}_3 + (2\text{NH}_3 + 2\text{H})$ and $\text{NH}_4\text{Cl} + \text{NH}_3\text{Li} = \text{LiCl} + \text{NH}_3 + (\text{NH}_3 + \text{H})$.

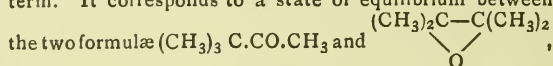
Chlorobromides of Thallium of the Type Tl_4X_6 .—V. Thomas.—Werner's hypothesis states that in the case of compounds of thallium of the type Tl_4X_6 , the thallium atom is placed in the centre of the group, and the two salts in question are stereoisomers:—



Mr. Cushman (*American Chemical Journal*, 1900, xxiv., 234) describes a method of preparation of these two isomers. The derivative α is stable, β being apparently characterised by its instability. The author repeats, with improved and altered details, all Mr. Cushman's experiments and draws certain interesting conclusions on the subject; these are described in detail in this paper.

Reactions of Trichloroacetic Acid.—A. Clermont.—When equal numbers of molecules of alcohol and trichloroacetic acid are mixed, and to this mixture a molecular proportion of monohydrated sulphuric acid is added, the heat evolved is considerable—sufficient to allow of the immediate formation of trichloroacetic ether. After some minutes the liquid becomes opalescent, and after the addition of four times its volume of cold water, the drops coalesce and a distinct layer is formed composed of ethyl-trichloroacetic ether. This can be separated and washed, and, on the addition of its own volume of ammonia, is rapidly converted into trichloroacetamide—a white crystalline body. This latter substance can be dried in the air and then sublimed, when it appears in brilliant plates and looks like naphthalene. These reactions, characteristic of trichloroacetic acid, allow of its qualitative identification in a very short time.

Researches on the Isomerisations of Pinacone and its Derivatives.—Maurice Delacré.—The author's last researches on the question of the constitution of pinacoline led him to believe that the hitherto accepted formulæ are insufficient. He describes the experiments which led him to this belief, and states as a conclusion that it is more reasonable to admit that pinacoline is a mixture, but not a mixture in the sense that is usually attributed to this term. It corresponds to a state of equilibrium between



and therefore preserves its claim to a chemical individuality.

Constitution of Piceol.—Ernest Charon and Démentrius Zamanos.—M. Tanret extracted from *Pinus picea* a glucoside (picein) decomposable by acids into glucose and piceol. He gives the empirical formula $\text{C}_8\text{H}_{10}\text{O}_2$ to piceol. The author, on examining this formula, believes it to be exactly that of a mono-oxyacetophenone, and such a hypothesis would explain the presence of the second oxygen atom in the molecule. His researches, which are described in this paper, demonstrate the correctness of this hypothesis. He prepares paraoxyacetophenone by other methods, and, using this and M. Tanret's piceol for various reactions, proves their identity.

MISCELLANEOUS.

Free Ammonia.—An ingenious and simple method of testing for free ammonia gas has lately been introduced by Mr. George Cockcroft, of Guy's Hospital. Many nitrogenous organic compounds when refluxed with caustic soda give off ammonia gas, which, as it is often accompanied by other vapours (volatile spirit, &c.) which disguise the characteristic odour, is not easy to recognise in small quantity. Mr. Cockcroft's method consists in using filter-papers soaked in a 7 per cent solution of CuSO_4 . One of these while still slightly moist is placed in the open end of the condenser at the beginning of the reflux distillation. The evolution of even slight traces of ammonia can then be detected by the appearance of a dark blue colour on the paper ("ammoniacal" copper sulphate). This is unlikely to be vitiated by other vapours, and the method is, under these conditions, less troublesome, more delicate, and more conclusive than tests by odour, fuming with HCl , &c.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 2nd.—Society of Chemical Industry, 8. "The Lemon Oil Industry," by Herbert E. Burgess and J. F. Child. "The Separation of Materials of different Specific Gravity," by J. W. Hinchley.

THURSDAY, 5th.—Chemical 8. Ballot for the Election of Fellows. Royal Institution, 5. General Monthly Meeting. "Influence of Substitution on the Formation of Diazoamines and Amino-azo-compounds," by G. T. Morgan. "The Determination of Available Plant Food in Soils by the Use of Dilute Solvents," by A. D. Hall and F. J. Plymen. "Some New Derivatives of Gallic Acid," by F. B. Power and F. Sheiden.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2193.

VOLUMETRIC ESTIMATION OF MANGANESE.

By HUGH RAMAGE, B.A., A.R.C.Sc.I.

It is gratifying to learn from the opening paragraph of Messrs. Ibbotson and Brearley's paper (*CHEMICAL NEWS*, vol. lxxiv. p. 247) that they have found the bismuthate method very satisfactory in practice. It is interesting also to learn that the rare metals, now used in the manufacture of certain special steels, do not interfere when present only in small quantities. Mr. Reddrop and the author did not anticipate the use of these rare metals. It is impossible to devise a rapid method of analysis which will apply, without modification, to all samples. The products of Sheffield include steels of all kinds, while we worked largely with mild steel and pig-iron.

It is unfortunate that only one of the points raised in Messrs. Ibbotson and Brearley's paper was dealt with, and that only partially, in the correspondence to which they refer. Some points mentioned in their paper must now be considered.

The original paper, by Mr. Reddrop and the present author, described one volumetric method for the analysis of wrought-iron, steel, and pig-iron. Messrs. Ibbotson and Brearley now refer to this as two processes, and include as a second the method of filtration, &c., employed in the analysis of ferromanganese and spiegel. There is no warrant for this in our paper. The original method gives accurate results when our instructions are followed (*CHEMICAL NEWS*, vol. lxxiv., pp. 209—210). The two methods of collecting the filtrate were fully discussed in 1891. As stated in my recent paper, we obtained results in close agreement with one another by both methods. This was evidently because we added only a slight excess of hydrogen peroxide, and, consequently, at the end of the filtration, the full quantity of ferric nitrate was in presence of only a very small quantity of hydrogen peroxide. The reason given for the selection of the method described was most assuredly the one which influenced me most.

The assertion in the third paragraph is more serious, namely:—"The statement in this footnote is untrue." Messrs. Ibbotson and Brearley have missed the point of this footnote. It was added to explain why the time of filtration should not exceed fifteen minutes. This is perfectly clear in the paper, and the second sentence of the footnote, which is not quoted, is:—"Where a very accurate result is desired, the analysis should be completed without unnecessary delay." The decomposition referred to was the time reaction, and our statement was based on the results of experiments.

The addition of an excess of from 1.5 to 3.0 c.c. of hydrogen peroxide was recommended to correct the small error caused by the decomposition of the permanganic acid. A reference to the amount used in the more refined method described in my paper—a bare working excess—will make this clear. This point also has evidently been misunderstood. The decomposition referred to in this was found by our later experiments to be similar in amount in Farnley iron (which is almost free from carbon), and in steels containing up to 0.09 per cent of carbon. It does not therefore appear to be due to combined carbon. It appeared from some results obtained in a series of experiments made in the early months of this year, that combined carbon was a cause of low results. This was before our discovery of the initial reaction between hydrogen peroxide and ferric nitrate. We therefore oxidised the carbon by addition of sodium bismuthate to the hot solution. Mr. Ibbotson consented to receive—and did re-

ceive—a full report of this series of experiments about the end of April.

The more refined method described in my paper may be used in the analysis of all samples of steel and pig-iron in which—when the shorter method is used—the final reaction is unsatisfactory. It will not, however, be found necessary, nor of any advantage over this shorter method, in the analysis of the mild steels which constitute the great bulk of our commerce.

Messrs. Ibbotson and Brearley recommend ammonium ferrous sulphate, or ferrous sulphate, as a substitute for hydrogen peroxide. Mr. Reddrop and the author were unable to find a satisfactory substitute for that reagent; ferrous sulphate was regarded as unsuitable, because the solution of permanganic acid is always saturated with oxygen, and smells slightly of ozone. It was presumed that ferrous sulphate would be oxidised by the dissolved gas; this was tested experimentally, and the presumption confirmed. The following is copied from the original notes:—"Twenty c.c. dilute nitric acid stirred with 1 grm. sodium bismuthate and filtered into 5 c.c. ferrous sulphate solution, required 3.7 c.c. N/10 potassium permanganate; reaction very sluggish. Five c.c. ferrous sulphate alone required 4.1 c.c. N/10 potassium permanganate."

No results are quoted by Messrs. Ibbotson and Brearley in evidence of the accuracy of the modification they propose. It is important to remark in this connection that, in working out new methods of analysis, results given by other methods should not be taken as standards unless the errors of these methods are duly considered. The results quoted in my recent paper are compared with absolute standards, and the agreement is very close.

In comparing the cost of this method with the cost of other methods, it would be fairer to take into account the saving in wages and the cost of all the reagents. The sodium bismuthate may be economised in different ways, but a good excess must always be present, for it is a solid reagent. For this reason, also, it should be allowed at least three minutes to oxidise the manganese, &c.

With regard to the paper by Mr. Du'ty, we considered the titration was more definite than a matching of tints. There is no reason, if great accuracy is not required, why the lead peroxide should not be replaced by sodium bismuthate in the ordinary colorimetric method. Filtration through asbestos would be much quicker than subsidence. This modification was suggested on two occasions in conversation with American chemists.

The experimental evidence before us is therefore in favour of the modifications of the bismuthate method recommended in our papers.

ACIDIMETRY OF PHOSPHORIC ACID BY MEANS OF BARYTA WATER.

By J. CAVALIER.

It is well known that if we titrate a solution of phosphoric acid with any given alkaline liquor, using methyl-orange or phthalein as indicators, the end-point of the first agent generally corresponds to the saturation of one atom of hydrogen of the PO_4H_3 , and the end-point of the second to two atoms. This is the case with the alkalis, soda, and potash; the end-point of methyl-orange is correct, but that of phenolphthalein is not correct; by reason of the hydrolysis of the dimetallic phosphate we are not able to observe the change of colour very sharply, but a slow end-point commences before the saturation of the second atom of hydrogen; this, however, is sufficient in the case of most titrations (*Joly, Comptes Rendus*, vol. cii., p. 317).

The results are very variable with the alkaline earthy bases; they depend not only on the dilution, but also on the manner in which the operation is conducted, and above all on the nature of the base.

I propose to examine the exact conditions necessary for

the use of the alkaline earths in the titration of free PO_4H_3 , and, if it is possible, to detect the corresponding end-point of saturation of the three degrees of acidity.

The results given were obtained with baryta.

End-point with Methyl orange.—If to a phosphoric solution (1 litre = $\frac{1}{10}$ th PO_4H_3) we add baryta water of moderate strength (1 litre = $\frac{1}{10}$ th BaO), the end-point with methyl-orange is good, the solution remains clear, the rose tint passes in a continuous manner to orange, and then becomes suddenly pale yellow; with a little practice this change can be observed very accurately; it corresponds to the addition of half a molecule of the base to 1 molecule of PO_4H_3 (the actual figures found were between 0.497 and 0.505).

A more concentrated solution ($\frac{1}{10}$ th) produces a gelatinous precipitate which re-dissolves in the acid liquor; it is important that this dissolution be complete at the moment of reading the end-point, otherwise the results will be too high; this can be effected by stirring or shaking sufficiently.

With a still greater concentration the complete resolution cannot be accomplished; we no longer obtain a solution at once limpid and neutral to methyl-orange, and the end-point can no longer be determined.

The neutral, clear solution obtained with a medium concentration contains $(\text{PO}_4\text{H}_2)_2\text{Ba}$, which decomposes spontaneously into PO_4H_3 and crystallised $\text{PO}_4\text{H}_2\text{Ba}$; the solution becomes rose coloured again after standing for a few minutes. This transformation is the more complete, and the state of equilibrium corresponds to a more acid liquid, as the concentration is greater and the temperature higher (Viard, *Bull. Soc. Chim.*, Series 3, vol. xix., p. 749); but even with the $\frac{1}{10}$ th solution it is not sufficiently rapid to interfere with the titration with methyl-orange.

The Use of Parantitrophenol as an Indicator.—Paranitrophenol, which is colourless in acid liquids, is yellow in an alkaline one. While Wieland (*Berichte*, vol. xvi., p. 1989) affirms that it is sensitive to CO_2 , and is thus similar to phthalein, Spiegel (*Berichte*, vol. xxxiii., p. 2640) shows, on the other hand, that it can *always* be used as an alternative to methyl-orange, over which it has the advantage of a very marked end-point which is easy to recognise without very much practice.

I have found that it can be used very effectively for titrating acids with the alkaline carbonates, but the end-point is much less distinct than with the caustic alkalis; the saturation of the acid is complete on the appearance of a pale-yellow colour; the intensity of the colouration then increases if we continue to add carbonate.

The saturation of phosphoric acid by a caustic base (soda or baryta) in the presence of parantitrophenol (two drops of a 2.5 per cent weak alcoholic solution to about 20 c.c. of the liquid) gives an analogous end-point; the commencement corresponds (though rather later) with the end of the methyl-orange reaction:—

I. 10 c.c. PO_4H_3 (1 mol. = 1 litre) required in normal NaOH:—

Methyl-orange up to yellow colour . . . 10.00 c.c.

p-Nitrophenol up to pale yellow colour . . . 10.05 "

II. 10 c.c. PO_4H_3 ($\frac{1}{10}$ th mol. = 1 litre) required in decinormal NaOH:—

Methyl-orange up to yellow colour . . . 10.05 c.c.

p-Nitrophenol up to pale yellow colour . . . 10.20 "

In the titration of phosphoric acid parantitrophenol can therefore be replaced by methyl-orange; the end-point is perhaps more easy to observe, but it is not quite so sensitive.

I might add that the greenish-yellow colour obtained does not interfere with the subsequent observation of the end-point of phthalein in the same solution.

End-point of Phthalein.—The figures in the following table show the amount of baryta (in molecules) which it is necessary to add to 1 molecule of acid to react with phthalein, while varying the conditions of the experiment.

	I. 1 litre = $\frac{1}{10}$ BaO. Mol.	II. 1 litre = $\frac{1}{10}$ BaO. Mol.	III. 1 litre = $\frac{1}{10}$ BaO. Mol.
The precipitate is entirely crystallised at the end of the operation carried out—	In the cold 0.997	1.005	1.003
	Hot 1.000	1.000	1.005
The precipitate is not entirely crystallised at the end-point. The total time of the titration being—	$\frac{1}{2}$ hour 1.17	1.08	—
	1 min. 1.22	1.17	1.14
	Less than 1 min. 1.35	1.19	1.15
The sudden addition of 1.5 BaO and back titration to decoloration of the phthalein—	— 1.36	1.23	1.49
	— 1.35	1.26	1.19

The nature of the end-point depends considerably on the method of conducting the operation.

It is very sharp when proceeding as recommended by Joly (*Comptes Rendus*, vol. cii., p. 318):—"The solution of baryta is run in until there is a distinct formation of a gelatinous precipitate; this consists of a tribarytic salt, which, on contact with the acid liquid, is transformed, either spontaneously or by stirring, into a crystalline precipitate of the bibarytic salt. By slowly adding baryta water we can obtain a fresh gelatinous precipitate which becomes transformed rapidly, and the operation is terminated when one drop of baryta gives an intense, persistent red colouration."

When the titration is carried out with baryta at $\frac{1}{10}$ th the length of the operation can be considerably shortened as follows:—The baryta is run in until the methyl-orange is just neutralised, and the clear solution is then heated; it rapidly gives an abundant crystalline precipitate, on contact with which the transformation is produced very quickly if we continue to add baryta.

With more dilute solutions the duration of the operation, which is practically the same hot or cold, is a little longer than in more concentrated solutions.

Whatever the dilution and temperature may be the precipitate can be obtained completely crystallised at the moment of the end-point, and therefore the latter is remarkably sharp; it requires, with great exactitude, the addition of 1 molecule of BaO (see the first two horizontal lines in the table).

The results are altogether different if the addition of baryta is made rapidly without waiting for the complete transformation of the gelatinous precipitate into the crystallised bibarytic one.

First of all, under these conditions, the end-point with phthalein is not distinct; we obtain transition tints with which it is impossible to observe a sharp change of colour. Then, at first the end-point is not persistent, the rose colour first obtained disappears in a few seconds on agitation. This should be compared with the observation made by Blarez (*Comptes Rendus*, vol. ciii., p. 265), that in the presence of a considerable amount of the base the quantity of baryta which combines with the phosphoric acid slowly increases with time.

The total amount of baryta which it is necessary to add to obtain an end-point persistent for some minutes, is always more than 1 molecule; the numbers found, evidently not very exact, are comprised between 1.08 and 1.25 molecules. The complete transformation into tribarytic phosphate requires 1.5 molecules. These figures become nearer to 1 as the stirring is more complete, the length of the operation greater, or the solution more dilute; all these conditions are precisely those which facilitate the formation of a crystalline precipitate.

We do not obtain any better result by suddenly adding 1.5 molecules of baryta to the phosphoric liquor (it is then strongly alkaline to phthalein), and then adding titrated

hydrochloric acid until the colour disappears. This shows the same characteristics as the direct titration; the end-point appears slowly, and after its first appearance the solution quickly returns to its red colour. On noting the moment when the decoloration persists for some minutes, the results found are higher than those given by direct titration with the same dilutions (1.19 to 1.36 molecules of BaO). But in no case, with the solutions used, do they approach 1.5 molecules, which corresponds with the total saturation of the three atoms of hydrogen in the PO_4H_3 .—*Bull. Soc. Chim.*, Series 3, xxv., No. 16.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Continued from p. 261).

PART II.—THE DETERMINATION OF URANIUM (continued).

Titration of Uranium Solutions with Potassium Permanganate.

ZIMMERMAN (*Liebig's Ann. Chem.*, 1882, ccxiii., 300) recommends, when uranous solutions are titrated with standard potassium permanganate solution, that the permanganate be added in excess, and the excess then titrated back with a standard solution of ferrous sulphate. He stated that by this procedure the oxidation of the uranous solution by air is prevented. In the following titrations—about sixty in number, and also a number of others made later—the recommendation of Zimmerman was not observed, but the uranous solution was titrated in the same manner as a ferrous solution. The oxidation of the uranous solutions was prevented by placing about 1 gm. of dry sodium carbonate in the large Erlenmeyer flask in which the titrations were made. The mouth of the flask was closed by a 2½ inch funnel, and the solution which was reduced in a small Erlenmeyer flask was emptied into it. The solutions, which were quite acid, on coming in contact with the dry sodium carbonate, liberated carbon dioxide which filled the "titration flask," and prevented the oxidation of the uranous solutions.

The reductions, whether made by metallic zinc, aluminum, or magnesium, were made in a small 250 c.c. Erlenmeyer flask, the mouth of which was closed by a small funnel. The uranyl solutions were poured into the flask, acidified, the metal added, and the reduction carried on at boiling temperature. After the reduction had occurred, the funnel and sides of the flask were washed down with distilled water, and the hot solution rapidly emptied into the "titration flask," which contained about 1 gm. of dry sodium carbonate. The flask in which the reduction was made was rinsed out four times with cold distilled water, the rinsings poured into the "titration flask," and the solution diluted to from 500 to 600 c.c. The titrations were made at once, adding the permanganate solution till pink "end-point," which was very delicate, when sulphate solutions were titrated.

The determinations were made as follows:—A measured amount of standard uranium nitrate solution was measured into a small beaker, and from 10 to 15 c.c. of sulphuric acid (sp. gr. 1.84), added. The solution was evaporated to dense white fumes, allowed to cool, then poured into an Erlenmeyer flask, which contained a small amount of water. The solution was diluted to a definite volume (100 to 200 c.c.), and more sulphuric acid added.

The best and most rapid reductions occurred when the amount of free sulphuric acid (sp. gr. 1.84) present was within the limits, 1 part acid to 4 parts solution, and 1 part acid to 5 parts solution. When the concentration is more than 1 to 4, the metal, especially zinc, is coated with

a rather insoluble sulphate which retards the generation of hydrogen.

Comparing the time required for the complete reduction of uranyl solutions with that required for the reduction of iron solutions, it was found to be about twice as long, when equivalent amounts of uranium and iron salts were reduced.

When zinc was the metal used for generating the hydrogen, about 50 grms. of pure metal (15 lumps) were used.

When the solutions were reduced by means of aluminum, fifteen strips of the metal were used, size 8 m.m. wide by 15 m.m. long, and 0.5 m.m. thick.

The reductions by means of metallic magnesium were made by using eight pieces of a bar 8 m.m. in diameter and 15 m.m. long.

The reductions, whether made by means of metallic zinc, aluminum, or magnesium, were in all cases the same. The only difference noticed was the rapidity of solution of the metals; aluminum dissolved more rapidly than zinc, and magnesium more rapidly than aluminum. The reduction, whether carried on at boiling temperature for one hour, or for as long as five hours, did not go further than $\text{U}(\text{SO}_4)_2$. The time required for the reduction of about 0.1 gm. of uranium by zinc is about one hour, for about 0.2 gm. not less than one and a-half hours. The uranyl sulphate solution, at first yellow in colour, changes to light green, and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which colour it retains even though the reduction be continued for as long as four hours.

The results, which were obtained by titrating uranous sulphate solutions, are all that can be desired, as they agree within analytical limits with those obtained by the standard gravimetric method, which is to precipitate the uranium with ammonia, and weigh it as U_3O_8 .

The reduction of hydrochloric acid solutions was also tried. For this purpose, a measured amount of standard uranium nitrate solution was twice evaporated to dryness with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry mass of uranyl chloride was taken up with 15 c.c. hydrochloric acid (sp. gr. 1.20), and water added, after which the solution was poured into a small Erlenmeyer flask, and diluted to from 100 to 200 c.c. More hydrochloric acid was added, and the solutions reduced at boiling temperature in the same manner as the sulphate solutions. The reductions were made first by the use of metallic zinc, then by metallic aluminum, and lastly by metallic magnesium. In all cases where the reduction was carried on for from two to four hours, it approached (and in several cases reached) the sub-chloride (U_2Cl_6 or UCl_3). With solutions of about 100 c.c. volume and rather strongly acid (1 part hydrochloric acid, sp. gr. 1.20, to 4 parts solution), at boiling temperature the reduction to UCl_3 was complete within about two hours. By longer treatment the reduction went no further. The colour of the hydrochloric acid solution of uranium, at first yellow, changed to green, to bluish-green, to olive-green, and finally to reddish-brown—resembling the colour of old port wine. The solutions, previous to titration, were cooled by running water, diluted to about 600 c.c., and titrated in the same manner as the uranous sulphate solutions.

The "end-point" was not so delicate as when sulphate solutions were titrated. As no "preventative solution" was added, a small amount of chlorine was evolved after the solutions were allowed to remain standing for a few minutes. The interference of the "end-point" by chlorine was prevented by having a very small amount of free hydrochloric acid present, not over 3 per cent of the total solution.

The results are given in Table VII. (Experiments Nos. 1 to 27).

The reduction of uranyl solutions to the uranous state can also be made by passing the solution through a Jones reductor. The reductor used was much longer than those

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxiii., No. 10.

TABLE VII.

Experiment No.	Dilution at reduction. C.c.	Time of reduction. Hours.	Dilution at the time of titration. C.c.	Amount of free acid present. C.c.	Amount of KMnO_4 required. C.c.	Uranium equivalent.	Theoretical amount of uranium taken.
<i>Reduction of Uranyl Solutions by Metallic Zinc.</i>							
1.	100	2 $\frac{3}{4}$	600	15 H_2SO_4	13'10	0'15406	0'15400
2.	200	3	600	20 "	13'15	0'15464	0'15400
3.	125	1 $\frac{1}{2}$	500	20 "	8'20	0'09643	0'09625
4.	135	1 $\frac{1}{2}$	500	25 "	8'20	0'09643	0'09625
5.	130	1	600	20 "	16'40	0'19286	0'19250
6.	130	1	600	20 "	16'35	0'19228	0'19250
7.	125	1 $\frac{1}{2}$	500	20 "	19'60	0'23050	0'23100
8.	125	1 $\frac{1}{2}$	500	25 "	19'65	0'23108	0'23100
9.	100	2 $\frac{1}{2}$	600	30 HCl	21'10	—	0'15400
10.	200	2 $\frac{3}{4}$	600	25 "	19'80	—	0'15400
<i>Reduction of Uranyl Solutions by Metallic Aluminum.</i>							
11.	110	$\frac{1}{2}$	600	15 H_2SO_4	13'15	0'15464	0'1540
12.	150	1 $\frac{1}{2}$	600	20 "	13'05	0'15350	0'1540
13.	150	2 $\frac{1}{2}$	600	20 "	13'10	0'15406	0'1540
14.	100	2 $\frac{3}{4}$	500	15 "	13'05	0'15350	0'1540
15.	100	3	500	15 "	13'10	0'15406	0'1540
16.	200	4	600	25 "	13'15	0'15464	0'1540
17.	120	1 $\frac{1}{2}$	600	30 "	13'15	0'15464	0'1540
18.	200	2 $\frac{1}{2}$	600	40 "	13'10	0'15406	0'1540
19.	200	2 $\frac{1}{2}$	600	50 "	13'15	0'15464	0'1540
20.	75	1 $\frac{1}{2}$	700	20 HCl	20'10	—	0'1540
21.	75	1 $\frac{1}{2}$	700	20 "	18'85	—	0'1540
22.	200	3	700	20 "	17'40	—	0'1540
23.	200	3	700	20 "	19'60	—	0'1540
<i>Reduction of Uranyl Solutions by Metallic Magnesium.</i>							
24.	125	1	600	20 H_2SO_4	13'10	0'15406	0'1540
25.	125	1	600	20 "	13'05	0'15347	0'1540
26.	125	2 $\frac{1}{4}$	700	20 HCl	16'90	—	0'1540
27.	125	2 $\frac{1}{4}$	700	20 "	17'60	—	0'1540
<i>Reduction of Uranyl Solutions by passing through Reductor.</i>							
		Minutes.					
28.	100	$\frac{1}{2}$	600	20 H_2SO_4	8'20	0'09643	0'09625
29.	100	9	600	15 "	8'20	0'09643	0'09625
30.	110	10	500	10 "	13'15	0'15464	0'1540
31.	110	10	500	10 "	13'05	0'15347	0'1540
32.	115	11	500	15 "	13'10	0'15406	0'1540
33.	115	11	500	15 "	13'10	0'15406	0'1540
34.	120	12	500	20 "	13'10	0'15406	0'1540
35.	120	12	600	20 "	13'10	0'15406	0'1540
36.	100	10	500	20 "	16'40	0'19286	0'1925
37.	100	10	600	20 "	16'35	0'19228	0'1925
38.	125	12	600	25 "	26'20	0'30810	0'3080
39.	130	14	600	30 "	26'20	0'30810	0'3080
40.	150	18	600	35 "	26'20	0'30810	0'3080
41.	110	15	600	15 "	16'40	0'19286	0'1925
42.	115	18	600	20 "	16'40	0'19286	0'1925
43.	135	20	600	25 "	26'20	0'30810	0'3080
Solutions Nos. 41, 42, and 43 were twice passed through the reductor.							
<i>Reduction of Uranyl Solutions by Stannous Chloride.</i>							
		Minutes.					
44.)	20	$\frac{1}{2}$	600	15	0'6—0'7	0'00823	0'1925
45.)							
46.)							
47.)	75	$\frac{1}{2}$	500	20	0'8—1'5	0'01764	0'1925
48.)							
49.)							
50.)	75	$\frac{1}{2}$	500	20	0'4—0'6	0'00706	0'1925
51.)							
52.)							
53.	35	1	550	35	0'8	0'00941	0'1925
54.	50	1	550	45	2'0	0'02352	0'1925
55.	35	5	600	35	16'0	0'18816	0'1925
56.	50	5	600	45	18'5	0'21756	0'1925
57.	75	10	600	10	4'0	0'04704	0'1925
58.	75	10	600	10	8'5	0'09996	0'1925
59.	35	10	600	25	11'0	0'12936	0'1925
60.	30	10	600	15	15'5	0'18228	0'1925
	30	15	600	15	20'9	0'24578	0'1925

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1901.

Professor McLEOD, F.R.S., Vice-President, in the Chair.

MESSRS. W. Lowson, E. Neumann, A. Findlay, E. Horton, G. Tatam, G. W. F. Holroyd, and S. E. Sheppard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Thomas Allen, 15, Sea View Terrace, Hartlepool; Arthur Baker, 130, Walmersley Road, Bury, Lancashire; Walter Craven Ball, 19, Lewisham Hill, S.E.; Andrew Russell Bennet, 1, Wildman Street, Nottingham; Harding Bickford, 46, Currie Street, Adelaide, S. Australia; Henry Boyers, 20, Knox's Street, Sligo; William Burton, Cotleigh, Nunnery Fields, Canterbury; William Cormack, 3, Westfield Place, Eskbank, Midlothian; Frank Crossley, Duchy Bank, Seedley Road, Pendleton, Manchester; John Howard Davidson, Golden Hill, Stoke-on-Trent; Francis Davis, Whitwell, Elland, Yorks; Robert English, 8, Colwall Villas, Burley Road, Beckenham, Kent; Eugène Arthur Fasnacht, Clayton Mount, Newton Heath, Manchester; Henry Wippell Gadd, 42, Union Road, Exeter; Hermann Charles Thomas Gardner, London Hospital, E.; Edward Gillman, Barbados, West Indies; William Peer Groves, Oldfield Hall, Altrincham, Manchester; Herbert Harding, 20, Stratford Road, Kensington, W.; Beresford Ingram, 19, Lewisham Hill, Lewisham, S.E.; Walter Henry Jollyman, Spartan House, Colney Hatch Lane, Muswell Hill, N.; James David Kettle, 1, Vardens Road, St. John's Hill, S.W.; Julian Bruce, Kingsmill, Ordnance College, Woolwich; Alfred Tabois Larter, 184, Holland Park Avenue, W.; Peter Macdonald, Lapstone Road, Millom, Cumberland; Lewis Jenkin Meyrick, 137, City Road, Birmingham; Charles Killick Millard, The Gilroes, Groby Road, Leicester; Albert Edward Parkes, 43, Whitehorse Street, Stepney, E.; Charles James Tomlin Pollitt, Athole, Church Street, Croydon, Sydney, N.S.W.; Charles Leonard Royle, Nellikuppam, South Arcot, India; John Henry Ryffel, 10, Onslow Gardens, Highgate, N.; George Charlton Scott, Eston Grange, Grangetown, R.S.O., Yorks; Edward Charles Sherwood, 39, Vincent Square, Westminster, S.W.; Norman Smith, 15, King Street, Bury; William Henry Templeman, 67, Park Street, Spring Bank, Hull; Harold Fay Fleetwood Varley, 22, Strathblaine Road, New Wandsworth, S.W.; Herbert George Wallace, Axim, West Africa; Philip Lewington Whitehouse, 32, Lawrence Street, Dowanhill, Glasgow.

Of the following papers, those marked * were read:—

*143. "Note on the supposed Formation of an Oxide of Hydrogen Higher than the Dioxide." By W. RAMSAY, F.R.S.

Bach (*Ber.*, 1900, xxxiii., 1506) has stated that evidence can be obtained of the existence of a peroxide of hydrogen higher than the dioxide by comparing the amount of oxygen evolved from peroxide on treatment with permanganate with the weight of the peroxide present in solution, as determined by titration with permanganate. It was suggested by Armstrong (*Proc.*, 1900, xvi., 154) that the discrepancy should be attributed to the formation of persulphuric acid and Caro's acid, due to the action of the peroxide on the sulphuric acid present during the titration. The author now showed that if peroxide be added to a mixture of sulphuric acid with permanganate, all the oxygen is evolved, but that if the permanganate be added to a mixture of peroxide with sulphuric acid, only a partial evolution of oxygen takes place, for neither persulphuric acid nor Caro's acid is readily attacked by permanganate. On the other hand, if acetic acid be substituted for sulphuric acid, the amount of oxygen evolved corresponds exactly with the amount of permanganate added, whether

ordinarily employed for the reduction of iron solutions. It was made of a 50 c.c. burette, in the lower part of which was placed an inch layer of broken glass, and on top of this was poured an 18 inch column of 20 mesh amalgamated zinc. The amalgamation was done by washing the tube with a warm dilute solution of mercurous nitrate, then thoroughly washing it with warm distilled water.

The determinations were made by taking a measured amount of standard uranyl nitrate solution, and evaporating it to dense white fumes with 10 c.c. sulphuric acid (sp. gr. 1.84). The solution was allowed to cool, then diluted to from 100 to 150 c.c., and more sulphuric acid added. The warm solution was poured through the reductor, and caught in a large Erlenmeyer flask, which contained about 1 gram of dry sodium carbonate, and the mouth of which was closed by a small funnel. After all the solution had been emptied into the reductor, it was followed by about 250 c.c. distilled water. The solution was then diluted to 500 c.c., and titrated with 0.01 normal potassium permanganate solution to faint red end-reaction.

The time required for 100 c.c. of uranyl solution and 250 c.c. of water to pass through the reductor was about ten minutes; for 150 c.c. uranyl solution and 250 c.c. of water to pass through it required about twenty minutes.

Sutton ("Volumetric Analysis," under "Iron") states that while washing the reductor free from iron solutions, the wash-water should be kept above the zinc level, so as not to allow of any air-spaces between the successive additions of water, in which case hydrogen peroxide is formed, thus causing high results. This caution was observed in the reductions.

The most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was not less than 1 to 6, nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of free sulphuric acid (sp. gr. 1.84) to total solution was within the limits of 1 to 6 and 1 to 5. Even when the solutions were twice run through the reductor no further reduction occurred than when run through once.

The results obtained are shown in Table VII. (Experiments Nos. 28 to 43).

Reduction of Uranyl Solutions by Stannous Chloride.

These reductions were made in the same manner as iron by the Zimmerman-Reinhardt method. In some of the reductions the stannous chloride was allowed to act much longer than is ordinarily done for iron; but with the majority the procedure was the same as for iron reductions.

The colour of the uranyl chloride solutions was yellow, but on continued boiling with stannous chloride it changed to green, and, on still further boiling, to reddish-brown. When the solutions were boiled with stannous chloride, a small amount of dry sodium carbonate was added to the flask, the mouth closed by a small funnel, and the boiling continued.

When the reductions were allowed to continue for a minute or so, as for the reduction of ferric solutions, a very slight reduction occurred, but when the reduction was continued for from fifteen minutes to half-an-hour, the reduction approached, and in several cases proceeded to the sub-chloride (UCl_3), the same as when a hydrochloric acid solution of uranium is reduced by either zinc, aluminum, or magnesium.

The uselessness of stannous chloride for the reduction of uranium solutions is shown in Table VII. (Experiments Nos. 44 to 60).

(To be continued).

the latter be added to a mixture of peroxide and acetic acid, or whether the peroxide be added to a mixture of permanganate and acetic acid.

*144. "The Electrolytic Reduction of Nitrourea." By G. W. F. HOLROYD.

Nitrourea can be reduced to semicarbazide much more easily if the reduction be effected by electrolysis than by the original method of Thiele and Heuser (*Ann.*, 1895, cclxxxviii., 311).

An aqueous solution of ammonium chloride serves as electrolyte. No porous cell is used. The reduction is effected at 20°. The poles are of iron or zinc. In the latter case an alternating current is employed to prevent the formation of a bridge of zinc from pole to pole. Four ampère-hours are required for the reduction of each grm. of nitrourea. The semicarbazide is precipitated as benzal-semicarbazone. The yield of re-crystallised benzal-semicarbazone is 60 per cent of the theoretical.

*145. "The Constitution of Pilopcarpine." Part III. By H. A. D. JOWETT, D.Sc.

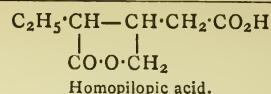
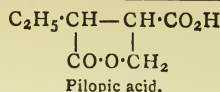
On a fuller examination of the products of the oxidation of isopilopcarpine with permanganate, it was found that, in addition to acetic and pilopic acids, small quantities of propionic acid and of a new acid named homopilopic acid, $C_8H_{12}O_4$, are formed. The formula $C_7H_{10}O_4$, previously proposed for pilopic acid, is confirmed both by analyses of various derivatives of the acid and by the determination of the molecular weight of the methyl ester.

Pilopic acid, $C_7H_{10}O_4$, melts at 104° (corr.) and is dextrorotatory $[\alpha]_D^{15} = +36.1^\circ$ in aqueous solution, with excess of alkali present $[\alpha]_D^{17} = +3.2^\circ$. Its methyl ester boils at 155—160° under 10 m.m. pressure, and at 275° under 757 m.m. Its barium salt, $(C_7H_9O_4)_2Ba$, is a microcrystalline powder readily soluble in water. The anilide, $C_7H_9O_3NHPh$, forms white flat pearly plates melting at 110°. The acid strychnine salt, $C_{21}H_{22}O_2N_2(C_7H_{10}O_4)_2$, is readily soluble in water and alcohol, sparingly soluble in ether, and melts at 120°. The diamide of the hydroxy acid, $C_7H_{14}O_3N_2$, formed by the action of ammonia on ethyl pilopate, occurs in acicular crystals, sparingly soluble in cold water or alcohol, freely soluble in these solvents when hot, and melts at 160°. The barium salt of the hydroxy-acid, $C_7H_{10}O_5Ba.H_2O$, is a microcrystalline powder freely soluble in water, $[\alpha]_D^{15} = +6.1^\circ$. *Homopilopic acid*, $C_8H_{12}O_4$, boils at 235—237° under 20 m.m. pressure, and is dextrorotatory, $[\alpha]_D^{21} = +45.4^\circ$, with excess of alkali $[\alpha]_D^{21} = +5.9^\circ$. Titration of the acid showed it to be a monobasic laëonic acid. Its ethyl ester boils at 210° under 10 m.m. pressure. The barium salt, $(C_8H_{11}O_4)_2Ba$, is very hygroscopic. The diamide of the hydroxy-acid, $C_8H_{16}O_3N_2$, forms well-defined prisms melting at 208°, fairly soluble in hot water, but sparingly soluble in cold or hot alcohol or cold water. The barium salt of the hydroxy-acid, $C_8H_{12}O_5Ba.H_2O$, is a microcrystalline powder stable in the air. The author showed that the piluic acid of Pinner and Kohlhammer (*Ber.*, 1901, xxxiv., 727) may possibly be a mixture of homopilopic with some pilopic acid. Repetition of previous experiments on the bromination of ethyl pilopate, giving rise to the formation of isobutyric acid, show that this acid is the product of a secondary reaction, and that the formula previously proposed (*Trans.*, 1900, lxxvii., 851) must be abandoned. Pilopic acid is not easily reduced by hydriodic acid, as no change occurs on heating to 210°.

Pilopic acid, when fused with potassium hydroxide at a high temperature, yields only one product—normal butyric acid. Fusion at a lower temperature produces a small quantity of a crystalline isomeric unsaturated acid melting at 190°, but the greater part of the acid is recovered unchanged.

Homopilopic acid on fusion with potash at a medium temperature, yields α -ethyltricarballic acid, $C_8H_{12}O_6$.

From a consideration of the results obtained, the following formulæ are proposed for pilopic and homopilopic acids:—

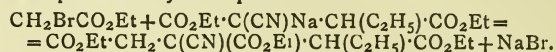


*146. "A New Synthesis of α -Ethyltricarballic Acid." By H. A. D. JOWETT, D.Sc.

α -Ethyltricarballic acid has been synthesised by the following reactions:—

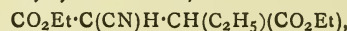
1. *Ethyl- β -ethylcyanosuccinate* was prepared by condensing the sodium compound of ethyl cyanacetate with ethyl α -bromobutyrate (compare Bone and Sprankling, *Trans.*, 1899, lxxv., 839).

2. The sodium compound of ethyl β -ethylcyanosuccinate was condensed with ethyl bromoacetate with formation of ethyl α -ethyl- β -cyanotricarballylate. This reaction may be represented by the equation—



3. *Ethyl ethylcyanotricarballylate* was hydrolysed with sulphuric acid; the resulting acid, heated at 180°, gave α -ethyltricarballic acid.

Ethyl β -ethylcyanosuccinate,—



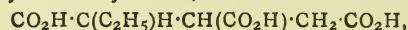
boils at 167—168° under 20 m.m. pressure, and has a density of 1.0647 at 15°/15°.

Ethyl α -ethyl- β -cyanotricarballylate,—



boils at 208° under 21 m.m. pressure, and has a density of 1.0972 at 16°/16°.

α -Ethyltricarballic acid,—



melts at 157°, the figure previously given by Michael (*Ber.*, 1900, xxxiii., 3745). The following new derivatives have been prepared:—The *anhydro-acid*, $C_8H_{10}O_5$, could only be obtained amorphous, and yields an amorphous compound with aniline; the *triethyl ester* is a colourless limpid liquid boiling at 170—175°. The *barium salt*, $(C_8H_9O_6)_2Ba_3.7H_2O$, is crystalline, and is more soluble in cold than in hot water. Only 6 molecules of water of crystallisation are lost at 180°. The *calcium salt*, $(C_8H_9O_6)_2Ca_3.9H_2O$, is characteristic, as its aqueous solution, on heating to 100°, becomes a firm jelly which liquefies on cooling. The *copper salt*, $(C_8H_9O_6)_2Cu_3.5H_2O$, is a greenish blue powder.

*147. "The Benzoylation of Fatty Acids in the presence of Ammonia; Formation of Amides." By K. J. P. ORTON.

On treating many monobasic fatty acids with excess of benzoyl chloride in the presence of ammonia and sodium hydroxide, the amides of the acids are formed together with benzamide. When methylamine is substituted for ammonia, methylamides are obtained. If the fatty acid and benzoyl chloride are heated together at 100—120° for two or three hours before treating with ammonia (or methylamine) and sodium hydroxide, the yield of amide is much increased and amounts in some cases to as much as 75 per cent of the acid used. When the acids possess hydroxyl or amino-groups, they are at the same time both benzoylated and converted into amides.

The following amides have been prepared by this method:—Phenylacetamide; *p*-nitrophenylacetamide; *p*-nitrophenylacetmethylamide, $C_6H_4NO_2 \cdot CH_2 \cdot CONHMe$, crystallises in long silky colourless needles (from water), m. p. 159°; *p*-benzaminophenylacetamide, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot CONH_2$, prepared from *p*-aminophenylacetic acid, crystallises from alcohol in small plates, m. p. 248°; *p*-benzaminophenylacetic acid, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$, prepared by the Schotten-Baumann method, forms tufts of needles, m. p. 205—206°; *p*-benzoxyphenylacetamide, $C_6H_5 \cdot CO \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CONH_2$, prepared from *p*-hydroxyphenylacetic acid, forms insoluble microscopic crystals, m. p. 167—169°; benzoylmandelic amide,

$C_6H_5 \cdot CH(O \cdot CO \cdot C_6H_5) \cdot CONH_2$, prepared from mandelic acid, crystallises from water in tufts of silky needles, m. p. 162° ; and *benzoylmandelic methylamide* in needles, m. p. 139° ; *cinnamic methylamide*, $C_6H_5 \cdot CH : CH \cdot CONHMe$, crystallises from water in plates, m. p. 111° ; *di-bromocinnamic methylamide* crystallises in lustrous prisms, which become coloured above 200° , melt and decompose at 214° . *Dibenzoyltyrosinamide*, $C_6H_5 \cdot CO \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(NH \cdot CO \cdot C_6H_5) \cdot CONH_2$, prepared from tyrosin, crystallises in aggregates of lustrous needles, m. p. 246° . Stearic amide is obtained from stearic acid.

It is probable that either a compound anhydride of benzoic and the fatty acid (or possibly a simple anhydride of the fatty acid) is first formed; with ammonia (or methylamine) the anhydride yields the amide of the fatty acid.

*148. "*Liquid Nitrogen Peroxide as a Solvent.*" By P. F. FRANKLAND, Ph.D., F.R.S., and R. C. FARMER, M.Sc., Ph.D.

A study of the properties of this liquid led to the following results:—Inorganic salts are not dissolved by nitrogen peroxide, and in most cases are unattacked. The liquid is a powerful solvent for organic compounds. It is a moderately inert reagent, but its activity is greatly increased by the presence of traces of water or of lower oxides. Most organic acids, as well as halogen and nitro-compounds and quinones, could be dissolved unchanged and recovered by evaporation. Hydroxy-compounds were generally, though not always attacked, phenol being converted to 2:4-dinitrophenol. Aniline derivatives were diazotised and some compounds were merely oxidised, as anthracene, which was completely converted into anthraquinone.

The electric conductivity of hydrochloric acid, as well as of a number of organic acids, was examined in this solvent, and found to be too small to be measured, showing that the liquid does not bring about electrolytic dissociation. A number of molecular weight determinations of dissolved substances were made by the ebullioscopic method. The constant for 1 grm.-molecule in 100 grms. of solvent was first determined by a series of experiments in which indifferent compounds (nitrobenzene, &c.) were used and found to be equal to 13.7. On extending the experiments to organic acids, these were found in many cases to be associated to double molecules. This was found to hold for acetic and benzoic acids and for several of their derivatives. Di- and tri-nitrophenol, on the other hand, gave their normal molecular weights.

*149. "*On an Incrustation from the Stone Gallery of St. Paul's Cathedral.*" By E. G. CLAYTON, F.I.C.

Around what is known as the Stone Gallery, at the base of the dome of St. Paul's Cathedral, is a balustrade of Portland stone, surmounted by a heavy coping-stone of the same material. Much of the surface of the stone is greatly "weathered," and is coated by a stratum of a grey or black substance, which in some places (especially on the under-side of the coping-stone) attains a thickness of three-quarters of an inch. This material, which is brittle and detachable with a knife, has a very rough and irregular surface, is stalagmitic in character, and, though differing in colour, in other respects resembles very closely some boiler deposits. It can easily be reduced to a fine grey powder, which, under the microscope, shows no morphological features indicating the presence of fun-goid or similar matter.

Some of this incrustation has been analysed, with the following results (see Table, next column).

Evidently, therefore, the substance is composed chiefly of calcium sulphate, hydrated, together with some siliceous matter. Calcium carbonate, which might have been expected to be present, is not one of the constituents. What, then, is the origin of the incrustation? In the immediate vicinity, there is no obvious source of gypsum

In 100 parts by weight :—

Water lost at 100°	2.06
" " 150°	22.48
Organic matter (carbon)	1.10
Lime	26.44
Magnesia	0.27
Ferrous oxide	1.31
Silica, sand, &c.	10.39
(Including combined silicic acid, SiO_2 , 2.33)	
Sulphuric acid (combined)	34.93
Phosphoric acid (combined)	1.02
Carbonic acid	none
Chlorine	trace
100.00	

Bases and radicles being combined, the composition is apparently as follows:—

Water (100°)	2.06
" (150°)	22.48
Carbon (soot)	1.10
Calcium sulphate	59.38
" phosphate	2.22
" silicate	1.63
Magnesium silicate	0.67
Iron silicate	2.40
Sand and uncombined silica	8.06
100.00	

or plaster. It cannot have been blown upwards from the bare leaden roof of the Cathedral or floor of the gallery. The stones of the balustrade are cemented, of course, with mortar. Still less likely is it that so much calcium sulphate has found its way from the neighbouring thoroughfares. The sand and soot may, to a great extent, be thus derived, and perhaps a small proportion of the calcium sulphate represents coal-ash transported by wind. But after a careful consideration of all the circumstances, and especially the characteristic appearance of the incrustation, it is suggested that the presence of the main component is principally due to two centuries' solvent and weathering action of rain, charged with sulphurous and sulphuric acids derived from the gases and smoke of innumerable surrounding chimneys. The action exerted by rain beating heavily against the stone, in that exposed situation, must be very considerable. The deposit of calcium sulphate, left by the water dripping and running from the under-side of the coping-stone, has become gradually thicker, just as is the case with stalagmite and calcareous tufa, to which the external features of the incrustation give it a curiously close resemblance. That the weathering influence of rain has been potent, no one examining the surface of the Portland stone can have a moment's doubt.

150. "*Note on Asbestos.*" By E. G. CLAYTON, F.I.C.

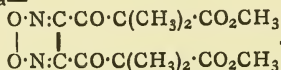
The following analyses of four kinds of asbestos (one of which, A, was stated to be of English origin, the remainder being examples of the ordinary mineral) are recorded for information and comparison, no published analysis of asbestos of English origin having been observed by the writer in any scientific journal.

Including the English specimen, all possess the general composition distinctive of true amphibole-asbestos, rather than asbestiform serpentine or chrysotile, which contains much more water and little or no lime. The English mineral consisted of moderately long, greyish-green fibres, easily separable, and in appearance resembling Italian asbestos, though characterised by unusual brittleness. B, C, and D, which had been pulverised before reaching the writer, were apparently associated with a little gypsum:—

	A.	B.	C.	D.
Water lost at 100°	1.19	0.87	0.86	—
" " 150°	0.05	0.13	0.00	—
" " a red heat..	0.70	0.95	1.83	—
Total water	1.94	1.95	2.69	1.39
Silica (with traces of man- ganese oxide, alkalis, &c.	60.88	48.48	59.82	61.74
Lime	11.11	6.19	5.91	6.91
Magnesia	10.84	35.52	28.27	25.72
Alumina	trace	4.69	1.25	2.30
Iron oxide.. ..	15.23	—	2.06	1.94
Sulphuric anhydride ..	—	3.17	—	—
	100.00	100.00	100.00	100.00

151. "The Action of Nitric Acid on Methyl Dimethyl-acetoacetate." (Preliminary notice). By W. H. PERKIN, Ph.D., F.R.S.

When methyl dimethylacetoacetate is heated with nitric acid of sp. gr. 1.145, vigorous action sets in, and if, when this has subsided, the product is thrown into water, a yellow oil separates, which on standing becomes semi-solid owing to the deposition of crystals. The crystalline product, when collected and purified by crystallisation from alcohol, melts at 65°, and gives numbers on analysis agreeing with those required for the formula $C_{14}H_{18}O_8N_2$. This new substance is decomposed by alkalis with formation of dimethylmalonic acid, isobutyric acid, hydrogen cyanide, carbon dioxide, and ammonia, and when treated with ammonia gives dimethylmalonamide. Its composition appears to be expressed by the formula—



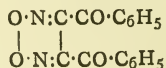
It reacts with semicarbazide, yielding a crystalline substance of the composition $C_{16}H_{24}O_8N_8$.

When the substance melting at 65° is reduced with tin and hydrochloric acid, it yields two colourless substances melting at about 154° and 173°, as well as a third substance which melts at 177°, and crystallises in primrose-yellow needles.

The two colourless substances are isomeric, and have the composition $C_{14}H_{20}O_8N_2$; the one melting at 154° gives a crystalline condensation product on treatment with semicarbazide, whereas the other, melting at 173°, does not.

The primrose-yellow substance (m. p. 177°) has the formula $C_{13}H_{16}O_5N_2$, and is much less soluble in alcohol than the colourless reduction products. It combines with semicarbazide and with phenylhydrazine. It dissolves in potassium hydroxide, forming an intense orange-red solution from which a colourless, crystalline acid, $C_{12}H_{14}O_5N_2$, separates on adding a mineral acid. This acid melts at 214°, yields a well characterised barium salt, $(C_{12}H_{13}O_5N_2)_2Ba$, and is re-converted by treatment with methyl alcohol and hydrochloric acid into the primrose-yellow substance, which is therefore its methyl ester. The constitution of the three reduction products will be considered in the detailed paper.

Substances similar in constitution to that obtained by the action of nitric acid on methyl dimethylacetoacetate have already been prepared in the aromatic series; thus Hollemann (*Ber.*, 1895, xxviii., 3360) obtained diphenyldinitrosacyl,—



by the action of concentrated nitric acid on acetophenone. Baum (*Ber.*, 1895, xxviii., 3211) also obtained a condensation product of similar constitution by treating acetylmesitylene with nitric acid.

152. "Note on the Displacement of Benzyl by Methyl in Substituted Nitrogen Compounds." By H. O. JONES, B.A., B.Sc.

In trying to effect the union of methyl iodide and dibenzylaniline, it was found that no action took place in the cold, but that on heating the mixture to 100° in a sealed tube only phenyltrimethylammonium iodide, unchanged dibenzylaniline, and benzyl iodide were obtained (*Proc. Camb. Phil. Soc.*, [2], xi., 114). On heating together dibenzylaniline and methyl iodide in the proportion of one molecule of the former to three of the latter to 100° for about two hours, a nearly theoretical yield of phenyltrimethylammonium iodide was obtained, the two benzyl groups having been eliminated as benzyl iodide.

It was of interest, in view of the fact that V. Meyer (*Ber.*, 1875, viii., 936) had shown that methyl iodide had no action on tetraethylammonium iodide, to see whether methyl iodide would displace the benzyl radicle in an ammonium compound. Phenylmethyldibenzylammonium iodide was, therefore, heated to 100° with methyl iodide, with the result that it was entirely converted into phenyltrimethylammonium iodide and benzyl iodide. The same displacement was effected in phenyldimethylammonium iodide and benzylaniline.

Experiments were made with ethyl, propyl, isobutyl, and allyl iodides on the above benzyl compounds; and with methyl iodide on other phenyl ammonium compounds; but at 100° no displacement was observed in any case.

The ready displacement of the benzyl radicle by methyl may be due to the "mobility" of the former, which is usually split off to some slight extent as iodide when a benzyl ammonium iodide is heated either in the dry state, or in aqueous or alcoholic solution, combined with the stability of phenyltrimethylammonium iodide, which is only decomposed at 220—225°. However, the non-displacement of benzyl by alkyl radicles other than methyl, and of such radicles as ethyl and propyl by methyl, suggests some peculiar relation (possibly stereo-chemical) existing only between the methyl and benzyl radicles.

NOTICES OF BOOKS.

Qualitative Chemical Analysis, Organic and Inorganic.

By F. MOLLWO PERKIN, Ph.D. With Nine Illustrations and Spectrum Plate. London, New York, and Bombay: Longmans, Green, and Co. 1901. Pp. 266.

ONE of the great difficulties in teaching chemistry is to get a combination of a book-student and a laboratory-student; the one acquires the whole of his knowledge from reading, and is quite at sea in the laboratory, while the other is practically ignorant of theoretical principles. The ideal student would be one who combined the two characteristics, not neglecting one for the other. The author, recognising this difficulty, has endeavoured to write a book, in which theory and practice run, so to speak, side by side. He admits, however, that the book is more of a practical than a theoretical one.

The volume is divided into two parts; I. on Inorganic Analysis, and II. on Organic Analysis.

Part I. commences with the Dry Reactions, followed by a chapter on Reactions in Solutions. In Chapter III. the division of the metals into groups is explained, but the author has departed from the usual custom of giving the group numbers, i., ii., iii., &c., but, instead, with a view to preserving their individuality, he calls them by the name of a characteristic element; thus, instead of group i. or group iv., we have "the silver-group" and "the iron-group." The following chapters deal *seriatim* with these groups and with the acids, and this part is concluded with the necessary analytical tables for the detection and separation of the metallic and acid radicals.

Part II. commences with the Qualitative Elementary Analysis of Carbon Compounds, followed by others on Organic Acids and Phenols, Aldehydes, Alcohols, the Sugars, the Alkaloids, &c. In the summary it is truly

pointed out that organic analysis is far more complicated than inorganic work, there being no simple set of tables for the former as there are for the latter. Organic chemistry is so intimately bound up with theoretical questions that it behoves the student to give much more time to book work than is necessary in the other branch of chemical science.

The book is well and clearly written and printed, and contains an index of seven columns.

Elementary Organic Analysis. The Determination of Carbon and Hydrogen. By FRANCIS GANO BENEDICT, Ph.D. Easton: The Chemical Publishing Company. Pp. 86.

BUT few elements are required to be determined in organic analysis, the most important being carbon, hydrogen, oxygen, and nitrogen; the latter being estimated by difference.

These operations require the minutest care and attention to detail to get anything like trustworthy results. Instructions with regard to these details are very often too vaguely given or hardly referred to at all in many textbooks.

In the volume now before us the author expresses the hope that the descriptions of processes here recorded will aid in making this method of analysis more familiar and satisfactory.

After a preliminary description of the necessary apparatus and absorbing agents, &c., the author gives detailed instructions for performing the combustions of various bodies, such as those containing nitrogenous substances, the halogens, sulphur, liquids, and volatile bodies, &c.; and finally, the combustion of explosive bodies. The book concludes with the calculation of results, an appendix, and an index.

Thirty-seventh Annual Report on Alkali, &c., Works. By THE CHIEF INSPECTOR. Proceedings during the year 1900. London: Eyre and Spottiswoode. 1901. Pp. 144.

THE number of works now registered under the A&Ts in England, Ireland, and Wales is 1054; of these 85 only are works decomposing salt; there are also 127 works registered in Scotland, bringing the total number of registered works to 1181. During the year, 4989 visits were made, and 5431 tests. It is to be regretted that as a result of these tests there has been no diminution in the number of prosecutions under the A&T, the number being five.

The average escape of acids of sulphur and nitrogen from exits of sulphuric acid works throughout the country shows a slight reduction from that for 1899, though being a fraction higher than the similar figures for 1897 and 1898. In several cases this year the stock of acid in the vitriol chambers has been drawn down to the very minimum required to lute the gases. Under such conditions the chamber reactions themselves are liable to be rapidly affected, changes taking place with extreme rapidity in the direction of disorganisation of the process and increase of escape, and requiring the utmost vigilance on the part of the management to keep under control.

Through the courtesy of manufacturers the Chief Inspector has been enabled not only to continue the table given for several years past on the produce of ammonia from all sources in the United Kingdom, but, by the sanction of those engaged in the recovery of by-products from coke ovens, to make this table more instructive by the inclusion of a new sub-head—ammonia recovered from coke ovens; the growth of this industry has been comparatively rapid of late years, and several new plants have started operations this year.

The results of the examinations of the chimney gases for hydrochloric acid at salt works has been very satisfactory; the limit allowed is one-fifth of a grain per cubic foot of escaping gases; the average actual escape has only slightly exceeding one-quarter of this amount.

It is evident that taking it all round the alkali industry is in a very satisfactory condition, in so far as concerns the care taken and the skill with which the operations are conducted. It is, however, to be regretted that there has been one explosion attended with loss of life; this was due to the accumulation of a mixture of explosive gases in a tar-well at a gas works in Lancashire.

Researches on the Past and Present History of the Earth's Atmosphere. Including the Latest Discoveries and their Practical Applications. By Dr. THOMAS LAMB PHIPSON. London: Charles Griffin and Co., Limited. 1901. Pp. 194.

THE science of the atmosphere is very far-reaching, and includes in its wide embrace not only meteorology but also the realms of physical geography, geology, chemistry and physiology, &c.

The author commences his interesting treatise from the very earliest times, when the probabilities are that there was no free oxygen in the air. The first free oxygen was due to the action of plant-life, and after many ages the atmosphere became fit for the lowest forms of respiratory life; as time went on less and less carbonic acid was present, while the proportion of free oxygen continually increased, until, finally, the author proposes this seeming paradox, that oxygen, which is admitted to be the product of life whilst it is the condition of life, will perhaps by its final predominance be the cause of universal death.

The second part of this volume deals with the atmosphere of our present period, from various points of view, both as to chemical constitution; physical properties, such as the odour in different countries, at sea, on land after a summer shower, &c.; electric phenomena; solid substances, which either fall like meteorites, or can be detected in suspension, and a host of other important matter.

The book consists of twenty-four chapters, all of which teem with interesting information and speculation; the whole being written in the author's well-known chatty style, which needs no further commendation from us.

Besides a full table of contents there is also a good index.

Painters' Colours, Oils, and Varnishes. A Practical Manual. By GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry; late Lecturer on the Technology of Painters' Colours, Oils, and Varnishes at the Municipal Technical School, Manchester. Third Edition, Revised and Enlarged. London: Charles Griffin and Co. Limited, Exeter Street, Strand. 1901.

THE demand for this manual having rendered a third edition necessary, the author has taken the opportunity of adding many recently acquired details of colour manufacture, thus bringing the subject up to date. There is no need to enlarge upon the thoroughly sound and practical character of the work, having already done so upon the issue of previous editions. Colour and varnish makers are to be congratulated upon having had the subject of their productions discussed in so clear and scientific a manner, and we feel sure that work of this kind will enable them in the end to dismiss many of their old "rule-of-thumb" methods as belonging to an age that has passed, and to place their manufactures upon a sound scientific footing, to the great advantage of both themselves and their customers. The book as heretofore is well illustrated and indexed.

The Chemistry of Paints and Painting. By A. H. CHURCH, F.R.S., M.A., D.Sc., F.S.A., Professor of Chemistry in the Royal Academy of Arts, London. Third Edition, Revised and Enlarged. London: Seeley and Co., Lim., 38, Great Russell Street. 1901.

THE third edition of Professor Church's book will be welcomed by painters and "picture makers" generally; the

plan of the earlier editions has not been altered, but many changes and additions have been made. In Chapter XXIV., on "The Study of Old Paintings and Drawings," a very interesting account is given of an examination of some of the valuable works in the National Gallery, furnishing adequate evidence of the instability of several favourite pigments largely used during the eighteenth and nineteenth centuries. Very many of the colours have failed, particularly the greens where verdigris was much in use.

As a result of recent experiments upon stability of pigments used in oil-painting, the colours more commonly used are classified in three degrees:—First, *permanent*; second, *liable to change*; and third, to be *definitely excluded from the palette*; this last includes the carmines, lakes, verdigris, indigo, and some few others. Accounts are given of the experiments of Professor Hartley, Professor Rood, Mr. Sampson, and Mr. Andrews, on water-colour pigments; also the report by Sir W. Abney and Dr. Russell to the Science and Art Department upon the same subject.

There is both a table of contents and a good index.

Introduction to the Study of Chemical Philosophy: The Principles of Theoretical and Systematic Chemistry. By WILLIAM A. TILDEN, D.Sc.Lond., Sc.D.Dub., F.R.S., Professor of Chemistry in the Royal College of Science, London. Tenth Edition. Completely Revised and Re-arranged, with Answers to Problems. London, New York, and Bombay: Longmans, Green, and Co., 39, Paternoster Row. 1901.

DURING the twenty-five years that have elapsed since the first edition of this work so many changes have taken place, so many fresh discoveries have been made and new theories propounded, that it has been found necessary to completely re-cast, and, in a large measure, to re-write this book, whilst retaining its general character.

A work of this kind by an author of such standing as Professor Tilden calls for little comment upon our part, but it is a great pleasure, amidst the multitude of books upon the teaching of chemistry that are brought to our notice, to find one that is not merely a *collection* of established principles and facts brought together for the benefit of the student, but rather the marshalling into intelligent order by a master mind of the fundamental principles and doctrines of the science, and their presentation to the student in such a manner as materially to assist him to "attain to the broad and philosophic views of chemistry as a whole." We only wish that there were more text-books of this stamp in circulation. The book comprises about 350 pages, exclusive of the "Answers to Problems," and is thoroughly indexed.

CORRESPONDENCE.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—The Fellows of the Chemical Society, on being balloted last April, decided by a large majority that the day and hour of meeting of the Society could be altered with advantage to an earlier hour than 8 o'clock. The Council decided that the meetings should be held at 5.30 p.m. on Wednesdays, but this did not suit a number of the Fellows who were in the minority, and they held an extraordinary meeting, the result of which was that the Council altered the meetings for November and December of this session to Thursdays at 8 o'clock, and decided to hold the meetings in January, February, and March on Wednesdays at 5.30 p.m. Now I see that a section of the Fellows have got the President to summon an extraordinary meeting in order to pass a resolution to

alter the meetings next January, February, and March to 8 o'clock on Thursdays.

Are the meetings of the Chemical Society held for the sole benefit of the London Fellows to the exclusion of those living at a distance from London, who, if the meetings were held at 5.30 p.m., could attend and return home the same night? This selfish and childish action of the minority is making the Society look ridiculous and undignified, and I hope all those Fellows living in London and in the country who can attend the meeting on December 12th, and who are in favour of the Society meeting at 5.30 p.m., will do so, and let the minority know that they are not going to rule the majority, and that they will demand a ballot of the whole of the Fellows.

I would suggest as a compromise that the meetings be held on Thursdays at 5.30 and 8 o'clock alternately.

The proposed modification of By-law XI. is an insult to those gentlemen who give their time to govern the Society, and practically a vote of no confidence in them.

Hoping that you will insert this letter in this week's issue of the CHEMICAL NEWS, I enclose my card.—I am, &c.,

A FELLOW OF THE CHEMICAL SOCIETY.

November 30, 1901.

A NEEDED REFORM IN CHEMICAL NOMENCLATURE.

To the Editor of the Chemical News.

SIR,—When chemistry adopted its modern system of nomenclature, when it tried to tell the composition of a substance instead of the name of the man who discovered it, a decided advance was made. Now another step should be taken in the same direction. Chemical laws as well as chemical substances should be appropriately named. An experience of several years has shown me how much unnecessary labour is put upon a student when he is compelled to learn what "Avogadro's" hypothesis is, or "Dalton's" theory, or "Gay-Lussac's" law, or any one of a number of others; while he could learn all these with little difficulty if they possessed descriptive names. There is a tendency in the right direction at the present time, and some of the more modern writers very properly give the law and not the discoverer the prominence; but there are still too many who lay undue stress on the old names.

It may be objected by some that the use of the discoverer's name is the only method we have of showing our respect for him; but even those who would urge such a thing would not advocate the use of "Glauber's" salt, or of any of the old names of chemical compounds merely for the purpose of perpetuating the memories of the pioneers of chemistry.

I have been impelled to call attention to this need by noticing that while some of the recent text-books adopt the more rational method, too many still adhere to the clumsy old way. It certainly would be a move in the direction of simplicity if chemical writers would agree to re-name some of the old laws and theories so that the names would correspond with others used in the science. —I am, &c.,

EDWARD BOOTH.

University of California, Berkeley.

November 10, 1901.

MANGANESE IN WATER.

To the Editor of the Chemical News.

SIR,—The letter from Mr. T. H. Byron in the CHEMICAL NEWS, vol. lxxxiv., p. 183, calls to my mind an analysis of water recently made by me. This water was from a spring whose healing virtues were in high repute among the people of the locality. It was supposed to be efficacious for all ills, from consumption to mange. As a matter of fact it does seem to possess considerable

therapeutic value. Analysis showed it to be a weakly alkaline carbonated water. The only unusual ingredient was manganese, which was present to the amount of 2 parts per million, calculated as MnO . The sediment from the water on standing consisted chiefly of iron hydroxide with a little manganese. As the manganese did not deposit to any appreciable extent on standing or boiling, it could hardly have been present as a bicarbonate, though it would naturally be calculated as such.

The result of this analysis led me to look up the subject of manganese in mineral waters, and I have found it reported in nearly seventy analyses of American waters, in nearly half of these, however, only as "trace." In one water 47 parts per million of manganese sulphate was given, and in three other cases over 20 parts, as sulphate, bicarbonate, and carbonate respectively. In numerous instances several of the analyses were by the same chemist, and I think it may be inferred that manganese is often present, but not estimated or looked for.

In Dr. Crook's recent work, "The Mineral Waters of the United States and their Therapeutic Uses," manganese is omitted from the list of ingredients of mineral waters, but is later mentioned briefly in the description of the components. Here it is alluded to as having been detected in a few springs, and it is added that "it is probably a useful auxiliary to iron in several springs, but its claims are not such as to entitle it to an important place in therapeutics."

Of late years some attention has been given to the value of manganese in therapeutics, but it still needs much investigation, and it is by no means impossible that the manganese present in some mineral waters may possess a real value.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University,
Lexington, Virginia, November 16, 1901.

NOMENCLATURE OF THE IONS.

To the Editor of the Chemical News.

SIR,—The paper by Dr. Walker printed in a recent issue of the CHEMICAL NEWS (vol. lxxxiv., p. 162), and dealing with the nomenclature of ionic chemistry, was exceedingly timely, and disposed admirably of most of the difficulties. There is one other term, however, the need of which will be felt by any one endeavouring to discuss the subject before his classes. A word is needed to express materials which are capable of undergoing ionisation.

The use of the term salt for such substances leads to confusion. It has indeed been pointed out that acids are simply salts of hydrogen and bases salts of hydroxyl. But in ordinary language we still require an expression for salt-like compounds which are neither acids nor bases, and the use of the term salt in this sense is so firmly established that it seems better to leave its significance unchanged. For materials which are salts in the wider sense, that is bodies which undergo ionisation, I have found the word *ionogen* very useful. The word electrolyte seems to be applied rather to the solution as a whole than to the substance dissolved. In any case it has the unfortunate property of conveying to the beginner the impression that it is a liquid in which ions are produced by the electric current, and are not present until the current is used.—I am, &c.,

ALEXANDER SMITH.

The University of Chicago.
November 14, 1901.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Sir Thomas Barlow, Bart., M.D., Mr. K. M. Chance, Sir Walter G. F. Phillimore, Bart., D.C.L., and The Hon. C. S. Rolls were elected Members. The special thanks of the Members were returned to Dr. Ludwig Mond, F.R.S., for a donation to the Fund for Experimental Research.

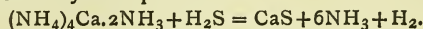
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiii., No. 20, November 11, 1901.

A New Method of Manipulation of Gases Liquefied in Sealed Tubes.—Henri Moissan.—The use of liquefied gases is becoming so common that the author makes a series of experiments on the precautions necessary for their preservation. During his experiments with Professor Dewar at the Royal Institution, fluorine was kept in a liquid state at a temperature of -80° , produced by the slow evaporation of a mixture of solid carbonic acid in ethyl alcohol. Careful experiments on this mixture show that a constant temperature of -85° can be produced by its slow evaporation. Solid carbonic acid and methyl chloride give a lower temperature (-90°), acetic ether saturated with solid carbonic acid gives -95° , and, finally, acetone, which dissolves a great quantity of the anhydride, goes down to -98° . A still lower temperature (-110°) may be obtained by cooling dry air by the rapid evaporation of the last freezing mixture. A still further reduction in temperature (-182.5°) is produced by the use of liquid air, or better liquid oxygen. When it is necessary to find the action of a liquefied gas on a solid, the pressure furnished at ordinary temperatures (if the critical point is high enough to maintain the liquid in the sealed gas tube) may be utilised. In order to seal the tube the liquid must be reduced to a solid state. Such tubes should be capable of sustaining a pressure of 200 to 300 atmospheres. The author uses crystal tubes 10 m.m. external and 6 m.m. internal diameter. In such tubes ammonia, chlorine, and sulphuretted hydrogen were preserved in the liquid state for years. The author finally mentions that all these manipulations are dangerous, and it is necessary to take the greatest care in handling glass tubes containing gases and liquids under these enormous pressures.

Action of Ammonium Metal on Sulphuretted Hydrogen.—Henri Moissan.—At a temperature somewhere between -75° and -70° the author allows liquid sulphuretted hydrogen to react on lithium-ammonium, giving lithium sulphide, ammonia, and free hydrogen. The molecule $(\text{NH}_4)_n$, if it is produced in this reaction, has no stability at this low temperature, and it decomposes into ammonia and hydrogen. He next allows liquid sulphuretted hydrogen to act on calcium-ammonium at the temperature of boiling sulphuretted hydrogen (-73°), when the same decomposition takes place. Calcium sulphide is formed and hydrogen evolved. From the weight of calcium before the experiment (0.0476 gm.) and the volume of hydrogen collected (25.87 c.c.) the reaction is apparently represented by the equation—



The theoretical quantity of hydrogen for the weight of calcium taken is 26.7 c.c. It was impossible to conduct these experiments at a lower temperature, the ammonia becoming solid at -75° . Ammonium, therefore, which hitherto has been only represented by a theoretical conception, apparently does not exist at the temperature of -73° in presence of liquid sulphuretted hydrogen.

Formation of Ozone.—A. Chassy.—When an electric current is passed through oxygen, ozone is formed in relatively small quantity. The proportion of ozone increases at first rapidly, but then tends towards a certain limit, as in the phenomena of dissociation. The author examines the manner in which the increase of ozone takes place in a definite mass of oxygen and having a perfectly constant current. The first important point which he establishes is that the law of the increase of ozone is the same whatever the intensity of the electric current. His

numerical measurements are given in the form of a table. The curve on which these numbers lie is asymptotic, the quantity of ozone tending towards a limit, which only depends on the temperature, and not on the intensity of the current, but which is difficult to determine with precision.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—

Professor J. A. Fleming, Six Lectures (adapted to young people) on "Waves and Ripples in Water, Air, and Ether."

Dr. A. Macfadyen, Six Lectures on "The Cell: its Means of Offence and Defence. Immunity."

Mr. W. N. Shaw, Two Lectures on "The Temperature of the Atmosphere; its Changes and their Causes."

Professor E. B. Poulton, Two Lectures on "Recent Researches on Protective Resemblances, Warning Colours, and Mimicry in Insects."

Dr. A. S. Murray, Three Lectures on "Recent Excavations at Delphi and in the Greek Islands."

The Rev. John Watson (Ian Maclaren), Three Lectures on "The Scot of the 18th Century: 1—At Home, 2—In Kirk, 3—With his Books."

Sir Henry Craik, Two Lectures on "Scotland's Contribution to the Empire."

Two Lectures on "Caricature in and out of Parliament," by Mr. E. T. Reed.

Four Lectures on "The Landmarks in the History of Opera: Gluck, Mozart, Weber, Wagner," by Mr. W. H. Hadow."

Six Lectures on "Some Electrical Developments," by Lord Rayleigh.

The Friday Evening Meetings will commence on January 19th, when Lord Rayleigh will deliver a Discourse on "The Interference of Sound." His Grace the President will, after the Discourse, unveil and present to the Institution, on behalf of the Subscribers, a Bust by Mr. Onslow Ford, R.A., of Sir Frederick Bramwell, Bart., Honorary Secretary of the Royal Institution from 1885 to 1900. Succeeding Friday Evening Discourses will be delivered by Mr. H. G. Wells, Professor A. Crum Brown, Professor Arthur Gamgee, Major P. A. MacMahon, Mr. W. Duddell, Professor Henry A. Miers, Professor H. Becquerel, Professor E. Ray Lankester, Geheimrath Professor Otto N. Witt, and other gentlemen.

The Energy of some Metallic Hydrates, Deduced from the Hydrolysis of the Salts.—G. Carrara and G. B. Vespignani.—The authors have measured this hydrolysis by means of the electric conductivity, on the one hand, and by means of the catalysis of acetate of methyl and the inversion of sugar, on the other hand. The conclusions to be drawn from the tables of the results are:—1. The basic energy of the metallic hydrates is in accordance with the position these elements occupy in the periodic system; this energy diminishes in the order, $Mg-Cu-Zn-Cd-Al-Fe$. 2. Hydrate of alumina is a more energetic base than ferric hydrate. 3. The basic ferric chloride is always much more hydrolysed than the sulphate, and this latter more than the basic sulphate of alumina. 4. Even in the presence of a considerable excess of potash, hydrated alumina only gives monopotassic aluminate. The di- and tripotassic aluminates are, at the dilutions at which the experiments were carried out, from $\frac{1}{2}$ to $\frac{3}{4}$ hydrolysed. 5. Hydrate of alumina is more basic than acid. Sulphate of alumina is hydrolysed fourteen times less than the aluminate. 6. The oxides of lead and zinc, dissolved in an excess of potash at the dilution $v=5$, form monopotassic plumbite and dipotassic zincate.—*Gazz. Chim. Ital.*, [2], vol. xxx., p. 35.

Contribution to our Knowledge of Indican.—H. Ter Meulen.—The indican used by the author was prepared from the leaves of the *Polygonum tinctorium* and the *Indigofera leptostachya*. These leaves, after immersion in boiling water for a few minutes, were systematically exhausted by warm water ($2\frac{1}{2}$ parts of water to 1 part of leaves); the liquid was filtered after precipitation by hot baryta water, and the separation of the excess of baryta by means of CO_2 ; it was then evaporated to dryness under reduced pressure; the residue was taken up with methylic alcohol, and the solution thus obtained treated with double its volume of ether, which precipitates various impurities. The ethero-methylic solution, when distilled, leaves a residue which, when taken up by water, gives crystalline indican in the form of small lance-like crystals, probably belonging to the orthorhombic system. Indican crystallises with $3H_2O$, and fuses at 51° ; when anhydrous it fuses at $100-102^\circ$; it is soluble in water, acetone, and methylic and ethylic alcohols, slightly soluble in C_6H_6 , $CHCl_3$, CS_2 , &c. It is levogyre (deviation about 2° for a 2 per cent solution, $l=200$ m.m.). If the solution be heated with hydrochloric acid and the indoxyl be eliminated by oxidation, the rotatory power becomes right-handed; the sugar formed by the hydrolysis of indican has not been characterised. Analyses and cryoscopic determinations enable us to confirm the formula given by Marchlewski for anhydrous indican, viz., $C_{14}H_{17}NO_6$, who considers it to be a glucoside, splitting up into glucose (1 molecule), and indoxyl (1 molecule).—*Revue. Trav. Chim. P.-B.*, vol. xix., p. 166.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). The Chemistry of Confedioners' Materials and Processes," by W. Jago, F.C.S., F.I.C.

WEDNESDAY, 11th.—Society of Arts, 8. "Aluminium," by Prof. Ernest Wilson, M.Inst.E.E.

FRIDAY, 13th.—Physical, 5. "On Circular Filaments and Circular Magnetic Shells Equivalent to Circular Coils, and on the Equivalent Radius of a Coil," by Prof. Thomas R. Lyle. "Air Pressures used in Playing Brass Instruments," by Dr. Barton and S. C. Laws. "A New Hygrometric Method," by E. B. H. Wade.

ST. THOMAS'S HOSPITAL MEDICAL SCHOOL.

JUNIOR DEMONSTRATOR OF CHEMISTRY AND PHYSICS.

The General Committee will shortly proceed to make this Appointment.

The Demonstrator will be required to devote his whole time to the teaching of Chemistry and Physics, under the direction of the Lecturer in Chemistry. Opportunity for Research Work will be afforded.

The stipend is £80 per annum and fees. Applications, with testimonials, should be sent to the Medical Secretary, St. Thomas's Hospital, S.E., not later than December 10.

H. G. TURNEY, M.A., M.D.(Oxon.), Dean.

Chemist (Ph.D., Vienna), wants fresh Appointment in Chemical Works or Laboratory. Experienced in Organic and Inorganic Chemistry; special knowledge and experience in Metallurgy. Small salary accepted until abilities proved.—Address, Dr. F. O., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Public Analyst has a Vacancy for a Pupil Assistant without Salary.—Address, B. F. H., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

RESEARCH CHEMIST.—Wanted for a Works in South of England, thoroughly trained Chemist, good at Research, Inorganic and Physical.—Address, with full particulars and terms, to "W. L.", care of J. W. Vickers, 5, Nicholas Lane, E.C. None but those with highest qualifications need apply.

GOVERNMENT GRANT to defray the expenses of Scientific Investigations. Applications for the year 1902 must be received at the Offices of the ROYAL SOCIETY not later than January 31st next, and must be made upon printed forms to be obtained from the CLERK TO THE GOVERNMENT GRANT COMMITTEE, Royal Society, Burlington House, London, W.

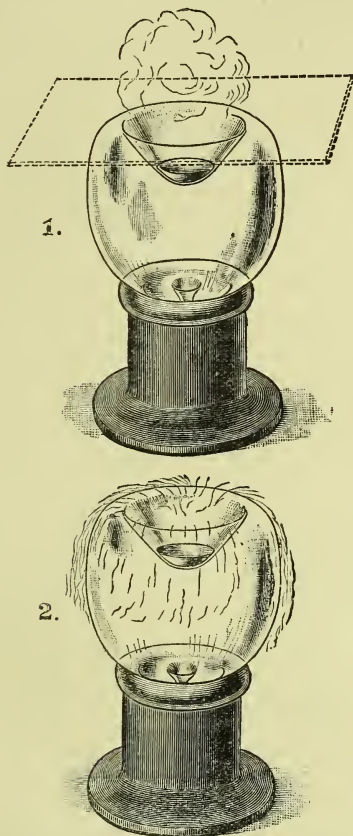
THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2194.

SOLID HYDROGEN.*

By Professor DEWAR, M.A., LL.D., D.Sc., F.R.S.

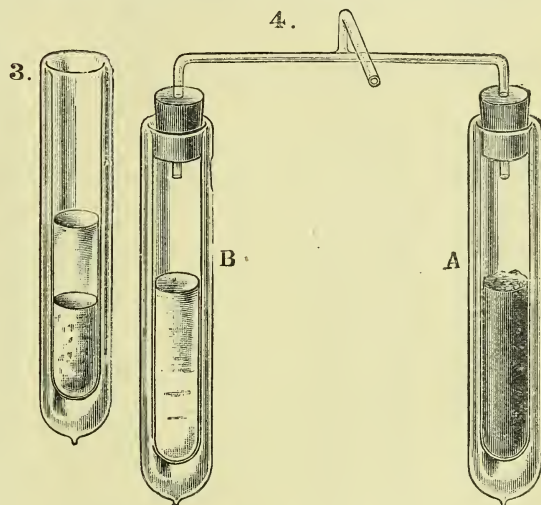
BEFORE proceeding to discuss the immediate subject of this lecture, it will be advisable to contrast experimentally some of the properties of hydrogen, nitrogen, and oxygen in the liquid condition. The two vacuum cups (Figs. 1 and 2), are charged half full respectively with liquid hydro-



gen and liquid air. When the cup containing the liquid air is placed in front of the electric lamp, the image thrown on the screen reveals the continual overflow of a dense vapour round the outer walls of the vessel. The saturated vapour coming from the steady ebullition of liquid air is three times denser than the free air of the room, and the result is it falls through that air just as if it were a dense gas like carbonic acid or ether vapour. To observe this phenomenon, the vacuum cup must be shallow, otherwise the vapour gets heated up before reaching the mouth of the vessel, and no difference of density in the air coming off is observed. We will now project the image of the cup containing liquid hydrogen, covered loosely in this case with a glass plate, upon the screen; here, no heavy vapour escaping round the sides is visible. The vapour of the boiling liquid hydrogen has a density nearly

equal to the air of the room, but as it gets very rapidly heated up by the glass cover the gas that is escaping is seen to rise in air like any light gas. On now removing the glass plate, a very different phenomenon is observed, which contrasts markedly with the behaviour of the liquid air in the former vessel. The cup and the air above is filled with a dense surging snowstorm of solid air; the air coming in contact with the excessively cold hydrogen vapour is suddenly solidified, and a part of it falls into the liquid hydrogen, causing more rapid evaporation, thereby intensifying the cloud condensation. After the mist has disappeared and all the liquid hydrogen gone, the cup contains a white deposit of solid air. This shortly melts, and on allowing the nitrogen to boil off, the presence of oxygen can be shown by the ignition of a red-hot splinter of wood. Such effects are easily understood when we remember that the boiling-point of hydrogen is proportionally as much below the boiling-point of air as the latter is below the ordinary temperature of this room.

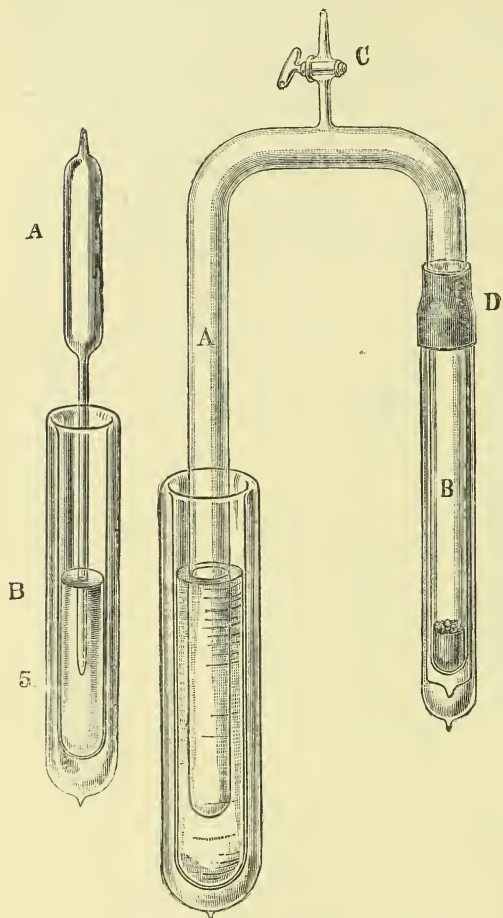
In order to observe the individual behaviour of the constituents of the air at temperatures below their ordinary boiling-points it is advantageous to place liquid nitrogen and oxygen in separate vacuum vessels, so connected that they may be simultaneously exhausted, as is represented in Fig. 4. On starting the air-pump both liquids enter



into rapid ebullition. As the exhaustion gets higher the temperature of each liquid gets lower and lower, and if the melting point is finally reached in either liquid it must shortly begin to solidify. This condition is quickly brought about in the case of the vessel A containing the liquid nitrogen, which passes rapidly into the condition of a dense white snow; but no amount of time spent in maintaining a good exhaustion (5 to 10 m.m. pressure) has any effect in changing the liquid condition of the oxygen in B. Oxygen, in fact, remains liquid at temperatures where nitrogen is solid. The snow of solid air produced by the evaporation of liquid hydrogen in the previous experiment, might thus be made up of solid nitrogen and a liquid rain of oxygen. To show that the temperature of boiling hydrogen solidifies oxygen, some of the latter liquid is placed in a vacuum test-tube C (Fig. 3), and liquid hydrogen H is poured on its surface, when the liquid oxygen is quickly transformed into a clear blue solid ice. Both oxygen and nitrogen, and we shall see later, hydrogen, can be changed into the condition of transparent ice as well as into the snowy state. A closed vessel filled with any gas at atmospheric pressure, of such a form that a portion of the surface in the shape of a narrow quill tube can be cooled in boiling liquid hydrogen like B, Fig. 5, shows condensation of the gas to the solid state; the only exceptions being helium and hydrogen itself. Here are two vessels of the

* A Discourse delivered before the Royal Institution, April 6, 1901

same shape as A, B, Fig. 5. The first contains helium showing no condensation when the part B is cooled; the second is filled with hydrogen, which equally shows no change of state under the conditions of the experiment. It is easy, however, to make the hydrogen vessel show liquefaction. For this purpose the experiment with the hydrogen is repeated, only before doing so the part A is heated to about 300°C . over a Bunsen burner, in order to increase the pressure of gas in the interior to above two atmospheres. Now liquefaction is seen to take place with great facility. No change is produced by similarly increasing the pressure in the helium vessel.



The extraordinary command liquid hydrogen gives us over the transition of state in matter may be best illustrated by the use of a new kind of cryophorus. Wollaston's celebrated instrument operates by forcing the evaporation of water in a closed vessel by condensing its vapour in a part of the receiver at a distance from the fluid, thereby causing a lowering of temperature in the latter until freezing takes place. Hence the name cryophorus or cold-bearer. Instead of using water we may now show that the same principle may be applied to the solidification of nitrogen at a distance, instead of water. The sole difference in this case is that the liquid nitrogen must be isolated from the influx of heat by being placed in a vacuum vessel and the condensation of its vapour must be effected by the use of liquid hydrogen.

No boiling-out operation is necessary with the cryophorus we are about to use. The apparatus is shown in Fig. 6. The vacuum tube B contains liquid nitrogen. It is fitted on by an indiarubber joint to a wide piece of glass

tubing doubly bent at right angles, A D; and in order to allow the gas from the boiling liquid to escape before the experiment begins, an aperture C is left which can be closed with a stopcock. On closing C, and inserting a part of the tube A into a vessel containing liquid hydrogen, the gas within is condensed, and thereby the pressure of the vapour in the interior of the vessel is reduced, forcing the liquid nitrogen in the other part of the apparatus to boil with great violence. In a few minutes the temperature of the nitrogen is so much reduced that it passes into the solid state. Many other liquid gases might be used to replace the nitrogen in this experiment. In making a selection, however, it is necessary to take only those bodies that possess a reasonably high tension of vapour at the melting point. The process would not succeed easily with a substance like oxygen, that has no measurable tension of vapour in the solid condition.

In the autumn of 1898, after the production of liquid hydrogen was possible on a small scale, its solidification was attempted by boiling under reduced pressure. At this time, to make the isolation of the hydrogen as effective as possible, the liquid was placed in a small vacuum test-tube, placed in a larger vessel of the same kind. Excess of hydrogen partly filled the annular space between the two vacuum vessels. On diminishing the pressure by exhaustion the evaporation was mainly thrown on the liquid hydrogen in the annular space between the tubes. In this arrangement the outside surface of the smaller tube was kept at the same temperature as the inside, so that the liquid hydrogen for the time was effectually guarded from influx of heat. With such a combination the liquid hydrogen was evaporated under diminished pressure, yet no solidification took place. Seeing experiments of this kind required a large supply of the liquid, other problems were attacked, and further attempts in this direction of producing the solid for the time abandoned. During the course of the present year many varieties of electric resistance thermometers have been under observation, and with some of these the reduction of temperature brought about by exhaustion was investigated. Thermometers constructed of platinum and platinum-rhodium (alloy) were only lowered 11°C . by exhaustion of the liquid hydrogen, and they all gave a boiling-point of -245°C ., whereas the reduction in temperature by evaporation *in vacuo* ought to be 5°C ., and the true boiling-point from -252°C . to -253°C . In the course of these experiments it was noted that almost invariably a slight leak of air occurred which became apparent by its being frozen into an air-snow in the interior of the vessel, where it met the cold vapour of hydrogen. When conducting wires covered with silk have to pass through indiarubber corks it is very difficult at these excessively low temperatures to prevent leaks, when corks get as hard as a stone, and cements crack in all directions. The effect of this slight air leak on the liquid hydrogen when the pressure got reduced below 60 mm., was very remarkable, as it suddenly solidified into a white froth-like mass like frozen foam. My first notion was that this body might be a sponge of solid air containing liquid hydrogen. The ordinary solid air obtained by evaporation *in vacuo* is a magma of solid nitrogen containing liquid oxygen. The fact, however, that this white solid froth evaporated completely at the low pressure without leaving any substantial amount of solid air, led to the conclusion that the body after all must be solid hydrogen. This surmise was confirmed by observing that if the pressure, and therefore the temperature, of the hydrogen was allowed to rise, the solid melted when the pressure reached about 55 mm. The failure of the early experiment must then have been due to supercooling of the liquid, which presumably is prevented by contact with metallic wires and traces of solid air. On the other hand, it is possible the pressure under which the ebullition took place might never have been low enough to reach the solid state.

(To be continued.)

ANALYSIS OF A SILURIAN LIMESTONE ROCK.

By Dr. T. L. PHIPSON.

THIS is one of the most ancient of stratified rocks; it is called in Herefordshire, whence my specimens were taken, by the name of "bastard limestone." On account of its large admixture with "old red" sandstone, it is not considered fit to produce lime for mortar. It forms a portion of the strata known to geologists as "lower Ludlow rock." The compact stone is brownish red, variegated with pale green and white, and passes into a schistous rock of a greenish grey colour containing as much as 60 per cent of sandstone. It yields a pink powder.

The specific gravity of the compact crystalline stone varies from 2.75 to 3.01. It is rather fragile, but is em-

The assays were first made by Patera's method as follows:—Eight samples of the finely divided ore (about 1.3 grms.) were weighed into small beakers, and decomposed by adding 5 c.c. water and 10 c.c. nitric acid (sp. gr. 1.42).

Complete solution was brought about by heating almost to boiling in covered beakers on a hot asbestos plate till the residues were almost white in colour, then the watch-glasses were removed, and the solutions slowly evaporated to a pasty mass. After cooling, the masses were taken up with 50 c.c. water and 3 c.c. nitric acid (sp. gr. 1.42), and the solution brought to boiling. The silica was filtered off and washed with boiling water, and rejected. The filtrates were diluted to 200 c.c. volume, and hydrogen sulphide gas passed through the cold solution for one hour. The precipitates of sulphides of lead,

Water, with some hydrocarbon gas	1.20—1.60	
Peroxide of iron	3.76	
Alumina	0.78	
Oxide of zinc	0.23	As silicate.
„ manganese	1.70	
„ nickel	trace	
Ceric oxide and rare earths	0.08	Separated as oxalates.
Titanic acid	0.12	As black titanite iron in the sandstone.
Vanadic acid	0.10	
Phosphoric acid	0.20	
Soluble silica	0.41	
Lime	30.69	
Magnesia	0.47	
Alkalis	0.03	
Tellurium	0.01	Probably as telluride of lead.
Gold	faint traces	
Lead	0.03	Found, oxide of lead 0.04.
Sulphuric acid	trace	
Chlorine	trace	
Quartz sand	34.00—32	(in compact stone) to 60 (in schistous rock).
Baryta	trace	
Carbonic acid (by difference)	26.19	Found, 25.96.
	100.00	

ployed on the farms for building purposes, &c. It contains a very large number of elements; the sandstone contains about 1 per cent of black titanite sand of a greater specific gravity. The analysis of the more compact portion of this rock has given me the accompanying figures.

The samples of this stone were taken about 2 feet from the surface in a quarry at Little Dewchurch, Herefordshire; it contains, dispersed throughout it, very minute tin-white specks which might be taken for mica, but which appear to be tellurium or telluride of lead.

THE QUANTITATIVE SEPARATION AND DETERMINATION OF URANIUM.*

By EDWARD F. KERN.

(Concluded from p. 273).

PART III.—ESTIMATION OF URANIUM IN PITCHBLEND.

In order to apply the preceding separations and determinations, to an actual technical assay of pitchblende, samples of the ore were analysed by two entirely different methods; the Patera method with modifications, and the "ether extraction" method. In both cases the uranium was determined in several different ways. These assays gave an actual comparison of results, and at the same time tested the separations and estimations of uranium which were worked out on pure solutions.

* Contribution from the Havemeyer Laboratories of Columbia University. From the *Journal of the American Chemical Society*, xxi.ii., No. 10.

copper, &c., were filtered, washed with hydrogen sulphide water, and rejected. The filtrates from the sulphides were at first slowly heated, and finally boiled in order to expel hydrogen sulphide gas and to oxidise the iron. Evaporation was continued till the bulk of the solutions was about 125 c.c., then the separated sulphur was filtered off and washed. The solutions were brought to boiling, and 150 c.c. of a saturated solution of sodium carbonate added, boiling was continued for twenty minutes, after which the precipitates (principally ferric hydroxide) were filtered off, and washed three times by decantation and four times on the filter with hot water. The filtrates containing the uranium were evaporated to half volume (about 150 c.c.), slowly neutralised with hydrochloric acid (sp. gr. 1.20), and about 3 c.c. in excess, then boiled for half-an-hour till all carbon dioxide was expelled. The uranium was precipitated from the hot solutions by means of a slight excess of sodium hydroxide (free from carbonate), and boiling for about ten minutes, keeping the beakers covered with watch-glasses. The orange-yellow precipitates of sodium uranate were allowed to settle, the supernatant liquids poured through filters, and the precipitates twice washed by decantation, and three times on the filters with hot water.

Precipitates Nos. 1 and 2 were dried in a hot oven, separated from the filters and ignited in platinum crucibles, after which the ash of the papers was added to the crucibles, and ignition continued at "redness" for five minutes. The residues on cooling were treated several times with hot water, after each treatment pouring the water through a small filter. The filters were dried, ignited, added to the crucibles, and re-ignited at "redness"

for ten minutes. After cooling in a desiccator, they were weighed. According to Patera, the residue consists of $\text{NaO} \cdot 2(\text{UO}_3)$, 100 parts of which contain 88.3 parts of U_3O_8 .

Precipitates Nos. 3, 4, 5, 6, and 7 were dissolved from the filters by warm dilute hydrochloric acid (sp. gr. 1.13), and caught in small beakers. The solutions were evaporated twice to dryness on a warm asbestos plate, the second time with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry residues were taken up with 3 c.c. hydrochloric acid, diluted to 100 c.c., and brought to boiling. The silica, dissolved from the beakers by the strong alkali solution, was filtered off, and washed with boiling water.

Solutions Nos. 3 and 4 were brought to boiling, 5 c.c. hydrochloric acid (sp. gr. 1.20) added, and ammonia (sp. gr. 0.90) in excess. The solutions were boiled for fifteen minutes, thus changing the voluminous amorphous precipitate of yellow ammonium uranate into a more crystalline form, darker in colour, which was readily and rapidly washed. The precipitates were allowed to settle, the supernatant liquids poured through filters, and the precipitates washed three times by decantation, and twice on the filter with a hot dilute solution of ammonium chloride (2 grms. of salt to 100 c.c. water). The precipitates were dried, placed in platinum crucibles together with filter-paper, and slowly ignited till the paper was completely destroyed, then ignited in a blast-flame for ten minutes, after which they were slowly cooled in a gradually decreasing Bunsen flame. During ignition the crucibles were placed in a slanting position in order to allow of free circulation of air in the crucible, thus obtaining complete oxidation to U_3O_8 . They were allowed to cool in a desiccator and weighed.

Solution No. 5 was diluted to 150 c.c., brought to boiling, and 5 c.c. hydrochloric acid (sp. gr. 1.20) added. The solution was neutralised with ammonia (sp. gr. 0.90) and 5 c.c. added in excess. Acetic acid was slowly added to the hot solution, stirring all the while, till the yellow precipitate disappeared. The uranium was then precipitated by means of ammonium dihydrogen phosphate, adding about twice as much as was necessary for complete precipitation. The solution was boiled for fifteen minutes, allowed to cool, then filtered, and the precipitate washed four times on the filter with a hot 2 per cent solution of ammonium chloride. The precipitate was dried, separated from the filter-paper which was first ignited in a porcelain crucible, after which the precipitate was added and ignited at low redness for ten minutes over a Bunsen flame. The crucible was allowed to cool, the residue moistened with a few drops of nitric acid (sp. gr. 1.42), dried on a hot plate, and re-ignited at low redness for ten minutes. The lemon-yellow coloured precipitate of uranyl pyrophosphate, $(\text{UO}_2)_2\text{P}_2\text{O}_7$, was weighed, and the U_3O_8 equivalent obtained by multiplying the weight by 0.66815.

Solutions Nos. 6 and 7 were evaporated to about 30 c.c. volume, allowed to cool, 30 c.c. sulphuric acid (sp. gr. 1.84) added, and evaporation continued to dense white fumes. The solutions were poured into 250 c.c. Erlenmeyer flasks, diluted to 150 c.c., and reduced at boiling temperature by about 50 grms. of pure granulated zinc. The reductions were continued for one and a-half hours till the solutions were a clear green colour. The solutions were then poured into a large Erlenmeyer flask, which contained about 1 gm. of dry sodium carbonate, diluted to 500 c.c., and titrated by 0.01 normal potassium permanganate solution.

Precipitate No. 8, of sodium uranate, was dissolved from the filter with warm dilute nitric acid (1 part acid, sp. gr. 1.42, and 2 parts water), and caught in a small beaker. The solution was evaporated to dryness twice, the second time with 10 c.c. nitric acid (sp. gr. 1.42). The dry mass was taken up with 5 c.c. of 50 per cent acetic acid, diluted to 50 c.c., and the solution boiled till all salts were dissolved. The silica, which was dissolved from the beaker by the strong sodium carbonate solution,

was filtered off, and washed with hot water. The solution was diluted to exactly 100 c.c. in a graduated flask, 50 c.c. were measured into a large clean platinum dish, and the uranium determined by electrolysis as follows:—Added 0.5 gm. sodium acetate, diluted to 125 c.c., and electrolysed at a temperature of 65° to 75° C., with a current of $\text{N.D.}_{100} = 0.8$ to 1.0 ampère. The uranium was completely precipitated, as hydrated protozestioxide, within eight hours. The electrolyte was emptied into a beaker, and the black deposit washed with warm water. The electrolyte and the washings were poured through a fluted filter-paper, the paper several times rinsed with hot water, dried and ignited on the cover of a platinum crucible, and the ash added to the dish. The dish was then dried, ignited over a blast-lamp for ten minutes, and allowed to cool in a gradually decreasing Bunsen flame. It was placed in a desiccator, and, after thoroughly cooling, was weighed. The ignited deposit consisted of U_3O_8 .

The results obtained by this series of assays are shown in Table VIII. (Experiments 1 to 13).

Estimation of Uranium in Pitchblende by the Ether Extraction Method.—The ether extraction method differs from the Patera method in that the uranium is not separated from the fourth group members by means of sodium carbonate, but by ether and by ammonium carbonate. The iron was separated from uranium and the other metals by shaking the hydrochloric acid solution with ether, free from alcohol. The uranium was then separated from the other associated metals (aluminum, manganese, zinc, and nickel) by means of ammonium carbonate.

The procedure was as follows:—Seven samples (about 1.3 grms.) of the finely divided pitchblende were decomposed with boiling dilute nitric acid (1 part acid, sp. gr. 1.42, and 1 part water) till the residues which remained were almost white in colour. The solutions were then evaporated to a pasty mass, taken up with 15 c.c. hydrochloric acid (sp. gr. 1.20), and evaporated to dryness twice, the second time with 10 c.c. hydrochloric acid (sp. gr. 1.20). The salts were taken up with 5 c.c. hydrochloric acid (sp. gr. 1.20), diluted to 150 c.c., brought to boiling, and the silica filtered off and washed. The filtrates were diluted to 250 c.c., and the lead, copper, &c., precipitated as sulphides by passing hydrogen sulphide gas through the cold solutions for about an hour. The filtrates from the sulphides were evaporated slowly to about 150 c.c., and boiled for a few minutes in order to expel all hydrogen sulphide. The separated sulphur was filtered off and washed. The solutions were brought to boiling, 5 c.c. nitric acid (sp. gr. 1.42) added, and boiling continued till the iron was completely oxidised, after which ammonia (sp. gr. 0.90) was added in excess, and boiling continued for fifteen minutes. The precipitates of impure ferric hydroxide, ammonium uranate, &c., were filtered off, and washed with a warm 2 per cent solution of ammonium chloride. The wet precipitates were dissolved from the filters with warm dilute hydrochloric acid (sp. gr. 1.10), and caught in small beakers. The solutions were twice evaporated to dryness, the second time with 10 c.c. hydrochloric acid (sp. gr. 1.20). The dry salts were taken up with 15 c.c. hydrochloric acid (sp. gr. 1.10), the beakers covered with watch-glasses, and the solutions heated till all salts had dissolved, but not long enough to lose any of the acid by evaporation. After cooling, the solutions were emptied into 250 c.c. separatory funnels, and the beakers rinsed out four times with 5 c.c. hydrochloric acid (sp. gr. 1.10). Fifty c.c. of pure ether which had previously been shaken up with hydrochloric acid (sp. gr. 1.10), were added to each funnel, and thoroughly shaken for about seven minutes with the aqueous hydrochloric acid solutions, occasionally relieving the pressure, due to evaporation of ether. After agitation, the funnels were allowed to stand for a few minutes till the two solutions separated, then the lower aqueous layers were run into other separatory

TABLE VIII.

Experiment. No.	Amount of ore taken. Grms.	Weighed as—	Weight. Grm.	Calculated to U_3O_8 equivalent.	Per cent of U_3O_8 .	Average. Per cent.
1.	1.2863	$NaO(U_2O_3)_2$	0.3064	0.27055	21.03	20.76
2.	1.3278	$NaO(U_2O_3)_2$	0.3071	0.27117	20.49	
3.	1.2882	U_3O_8	0.2616	0.26160	20.31	20.46
4.	1.2880	U_3O_8	0.2653	0.26530	20.60	
5.	1.2840	$(UO_2)_2P_2O_7$	0.3297	0.25940	20.20	20.20
6.	1.4004	Titrated	—	0.29090	20.77	
7.	1.2164	Titrated	—	0.24940	20.50	20.63
8.	0.6416	U_3O_8	0.1306	0.13060	20.36	
9.	1.2405	U_3O_8	0.2565	0.2565	20.67	20.61
10.	1.2409	U_3O_8	0.2550	0.2550	20.55	
11.	1.2390	$(UO_2)_2P_2O_7$	0.3233	0.2545	20.54	20.66
12.	1.2991	$(UO_2)_2P_2O_7$	0.3431	0.2701	20.79	
13.	2.2892	Titration	—	0.2672	20.80	20.71
14.	1.2828	Titration	—	0.2646	20.63	
15.	0.6207	U_3O_8	0.1283	0.1283	20.67	20.67

funnels. The ether layers containing most of the iron, were twice shaken up with 5 c.c. hydrochloric acid (sp. gr. 1.10), and the washings added to the main solutions containing the uranium. The second extractions were made with 50 c.c. ether, and the third with 30 c.c. ether. In both cases the ether solutions were twice washed with 5 c.c. hydrochloric acid (sp. gr. 1.10). The aqueous hydrochloric acid solutions, now free from iron, contained a small amount of ether, which was allowed to evaporate spontaneously by exposure. They were then evaporated to about half volume (40 c.c.), diluted to 100 c.c., nearly neutralised with ammonia, and 100 c.c. of a saturated solution of ammonium carbonate added, which precipitated all the metals except uranium. The solutions were slowly boiled for five minutes, filtered, and the precipitates washed with hot water. The filtrates were evaporated to half volume in order to get rid of most of the carbon dioxide. Yellow precipitates of ammonium uranate separated during boiling, and were dissolved by acidifying the solutions with hydrochloric acid. The solutions were again boiled for about half-an-hour longer, and the uranium determined in four different ways as outlined below.

Solutions Nos. 9 and 10 were precipitated with ammonia in the same manner as solutions Nos. 3 and 4, and the uranium weighed as U_3O_8 .

Solutions Nos. 11 and 12 were precipitated by an excess of ammonium dihydrogen phosphate the same as solution No. 5, and the uranium weighed as $(UO_2)_2P_2O_7$.

Solutions Nos. 13 and 14 were evaporated with sulphuric acid, reduced by metallic zinc, and titrated by potassium permanganate as described under Nos. 6 and 7.

In solution No. 15, the filtrate from the ammonium carbonate precipitation was evaporated to dryness with nitric acid, and the uranium determined electrolytically as already described under No. 8.

The results obtained by the ether extraction method are given in Table VIII. (Experiments 9 to 15).

A comparison of these results with those obtained by the Patera separation shows greater uniformity here. The close agreement is proof not only of the superiority of the ether extraction method, but also of the accuracy of the methods of determination of uranium already described.

Summary of Results.

The conclusions drawn from this investigation on the separation and determination of uranium, briefly stated, are as follows:—

1. In order to separate uranium (and the other members of Group 4) from the metals of Groups 5 and 6, the solution should contain not over one part of concentrated acid (either hydrochloric or nitric acid) in fifty parts of solution.

2. The separation of uranium from the metals of Groups 3 and 4 is best accomplished by means of either a saturated solution of sodium carbonate, or else by ether

followed by a saturated solution of ammonium carbonate. The latter method is preferable when the introduction of fixed alkalis and silica is undesirable.

3. The ether extraction method for the separation of uranium from iron depends on the fact that ferric chloride is extracted from an aqueous hydrochloric acid solution, whereas the uranyl chloride is retained in the aqueous solution. For this separation it is necessary that the hydrochloric acid used for the solution be of 1.10 specific gravity, and that three ether extractions be made. The ether used should be free from alcohol, and also previously shaken up with hydrochloric acid (sp. gr. 1.10).

4. The separation of uranium from iron by means of sodium carbonate is complete, provided a large excess of a saturated solution of sodium carbonate be used, and the solution boiled for at least fifteen minutes after the precipitation. The boiling is necessary in order to get all the uranium into solution. By such treatment, no uranium remains with the iron, which is completely precipitated as ferric hydroxide in a form readily filtered and washed.

5. The separation of uranium from the alkalis and alkaline earths by means of electrolysis is complete, easily accomplished, and gives accurate results.

6. The separation of uranium from the alkalis and alkaline earths is accomplished by precipitating the uranium three times from a hot solution with ammonia in the presence of ammonium chloride.

7. The separation of uranium from the alkalis and alkaline earths by means of an excess of ammonium phosphate in the presence of ammonium acetate is complete. The precipitations should be made from a hot solution, and the boiling continued for at least fifteen minutes.

8. The yellow slimy amorphous precipitate of an ammonium uranate, formed by precipitating uranium with ammonia in the presence of an ammonium salt, is converted into a darker crystalline form by boiling it for about twenty minutes, and then allowing it to settle in the cold.

9. The separation of the filter-paper from the precipitate of ammonium uranate for the purpose of igniting to UO_2 or U_3O_8 is unnecessary.

10. The complete oxidation of uranium to U_3O_8 is accomplished by igniting ammonium uranate, in either a platinum or porcelain crucible, over a blast-lamp. This is done by having the crucible in a slanting position, and igniting intensely over a blast-lamp for about ten minutes, after which the crucible is allowed to cool in a slowly decreasing Bunsen flame.

11. The reduction of U_3O_8 to UO_2 , as recommended by Rose for the purpose of control, was found unreliable.

12. The estimation of uranium as phosphate is easily and accurately done when the precipitant used is ammonium phosphate, in the presence of ammonium acetate. The precipitate of $UO_2NH_4PO_4$ on boiling becomes crystalline, and is easily filtered and washed. The ignited precipitate previous to weighing should be

moistened with nitric acid (sp. gr. 1.42), dried, and re-ignited at low redness in a porcelain crucible. Above this temperature, and especially so in platinum, a reduction of the $(\text{UO}_2)_2\text{P}_2\text{O}_7$ always occurs. Whenever this happens it may be re-oxidised to $(\text{UO}_2)_2\text{P}_2\text{O}_7$ by moistening the greenish mass with nitric acid (sp. gr. 1.42), and re-igniting at low redness. The ignitions should be done in porcelain.

13. The most rapid determination of uranium is accomplished by reducing a sulphate solution by means of pure metallic zinc, and titrating it with standard potassium permanganate solution in an atmosphere of carbon dioxide. The reductions, whether made by means of metallic zinc, aluminum, magnesium, or in a long Jones reductor, were in all cases complete, and the results obtained were concordant with those obtained gravimetrically.

14. When hydrochloric acid solutions of uranium are reduced by means of metallic zinc, aluminum, or magnesium, the reduction goes lower than UCl_4 . It approached and in several cases reached the sub-chloride UCl_3 . When stannous chloride is used the results are utterly unreliable; so no reduction of uranium in an hydrochloric acid solution can be used for the estimation of uranium.

This work was suggested by Dr. Edmund H. Miller, and carried out under his direction.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

MESSRS. R. Lloyd Whiteley and H. A. Tozer were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Geoffrey Black, 9, Routh Road, Wandsworth Common, S.W.; Harry Burrows, The Green, Southgate, N.; Frederick Edward Catchpole, 11, Jerningham Road, New Cross, S.E.; James Ward Daniels, Westwood, Medomsley R.S.O., Co. Durham; Frederick Davis, "Stanley," Whalley, nr. Blackburn, Lancs.; Charles Dorée, 87, Gore Road, London, N.E.; Clarence J. Green, B.Sc., 24, Dalberg Road, Brixton Church, S.W.; Ernest Bowman Luddam, University College, Bristol; Sydney Glyde Stephen Panisset, 7, Jersey Road, Strood, Rochester; William Charles Ross, 27, Pitt Street, Edinburgh; Francis Bernard Stead, Clifton College, Bristol; Arthur James Webb, 21, Hammelton Road, Bromley, Kent; Charles Edward Womersley, Kilpin Hill, nr. Dewsbury, Yorks; and of Messrs. T. K. Gajjar, Gingaum, Bombay; J. S. Jameson, Durban, Natal; Albert William Denis Leahy, Darjeeling, India; and Walter Herbert Pay, Durban, Natal, authorised by the Council under By-law I. (3).

Of the following papers, those marked * were read:—

*153. "On the Hydrochloride of Thiocarbamide." By H. P. STEVENS.

The hydrochloride of thiocarbamide, $\text{CSN}_2\text{H}_4\text{HCl}$, may be obtained directly by dissolving thiocarbamide in an excess of warm concentrated hydrochloric acid. On cooling, the salt separates out in large compact crystals, which have a strongly acid reaction, melting, with decomposition, below 100° , and are readily soluble in water and alcohol. They react with the latter solvent when warmed to form, probably, in the first case, ethyl chloride, which, combining directly with thiocarbamide, yields the hydrochloride of ethyl-pseudo-thiocarbamide in white prisms.

The method of Glutz for the preparation of thiocarbamide hydrochloride yields a very impure product, due

partly to loss of hydrochloric acid on concentration, and partly to the salt reacting with alcohol during re-crystallisation.

*154. "The Constituents of the Essential Oil of *Asarum Canadense*." By F. B. POWER and F. H. LEES.

In a previous investigation of this oil by one of the authors (Power, *Inaug. Diss. Strassburg*, 1880; *Proc. Amer. Pharm. Assoc.*, 1880, xxviii., 464) it was found to contain a terpene, $\text{C}_{10}\text{H}_{16}$; two fragrant alcohols, b. p. $196-199^\circ$ and $222-226^\circ$, both having the composition $\text{C}_{10}\text{H}_{18}\text{O}$; a nearly inodorous body, b. p. $254-257^\circ$, which, on oxidation with chromic acid, afforded a crystalline acid, $\text{C}_9\text{H}_{10}\text{O}_4$, the latter having since been shown to be veratric acid by Petersen (*Ber.*, 1888, xxi., 1062), who has also identified the substance affording it as methyleugenol; a deep blue oil collected at $275-350^\circ$; a large amount of acetic acid combined with the alcohols of the oil in the form of esters, and a very small amount of a less soluble oily acid which was believed to contain valeric acid.

The present investigation has shown the oil to have a much more complex composition than was at first supposed. The authors have now identified the following compounds, most of them by well-defined crystalline derivatives:—(1) A phenol, $\text{C}_9\text{H}_{12}\text{O}_2$, having a creosote-like odour; (2) pinene (nitroschloride, m. p. $103-104$, and nitropiperidine, m. p. $118-119^\circ$); (3) *d*-linalool (citral and citryl- β -naphtho-cinchonic acid, m. p. $195-198^\circ$); (4) *l*-borneol (camphor, m. p. 175° , $[\alpha]_D = -40.3^\circ$, and oxime, m. p. $115-116^\circ$); (5) *l*-terpineol (a ketolactone, $\text{C}_{10}\text{H}_{16}\text{O}_3$, m. p. $62-63^\circ$; terebic acid, $\text{C}_7\text{H}_{10}\text{O}_4$, m. p. $173-174^\circ$; and dipentene dihydride, $\text{C}_{10}\text{H}_{18}\text{I}_2$, m. p. 80°); (6) geraniol (diphenylurethane, m. p. $81-82^\circ$, and citral); (7) methyleugenol (bromomethyleugenol dibromide, $\text{C}_6\text{H}_2\text{Br}(\text{OCH}_3)_2\text{C}_3\text{H}_5\text{Br}_2$, m. p. $78-79^\circ$; it is also shown that methylisoeugenol does not exist in the oil); (8) a blue oil, boiling above 260° , and consisting of oxygenated compounds of undetermined composition but of alcoholic nature; (9) a lactone, $\text{C}_{14}\text{H}_{20}\text{O}_2$, having a very aromatic odour, but present in the oil in very small amount; (10) palmitic acid; (11) acetic acid; (12) a mixture of fatty acids, $\text{C}_6\text{H}_{12}\text{O}_2$ to $\text{C}_{12}\text{H}_{24}\text{O}_2$. The acetic acid is contained in the oil in the form of esters, whilst the higher fatty acids are in a free state.

A quantitative determination of the principal constituents was made. The amount of methyleugenol, determined by Zeisel's method, was found to be 36.9 per cent. The amount of esters, calculated as $\text{C}_{10}\text{H}_{17}\text{C}_2\text{H}_3\text{O}_2$, is 27.5 per cent.; the free alcohols, $\text{C}_{10}\text{H}_{18}\text{O}$, 13.3 per cent. The amount of pinene obtained by direct fractionation of the oil was about 2 per cent, and the amount of high boiling constituents, such as the blue oil, is therefore about 20 per cent.

DISCUSSION.

The PRESIDENT inquired as to the difference between *Asarum* and *Serpentaria*, the *A. Canadense* being known as Canada snake-root, whereas *Serpentaria* was called Virginia snake-root.

Mr. DAVIS pointed out that Kremers had recently shown (*Pharm. Review*, 1901, xix., 200) that the dark colour of the oil of wild bergamot (*Monarda fistulosa*) is due to small quantities of thymoquinhydrone formed by oxidation from thymoquinol, and asked whether the dark blue colour of the higher boiling-point fractions of the oil obtained by the authors might not be caused by the presence of a quinhydrone.

Dr. POWER replied that although both *Asarum* and *Serpentaria* belong to the *Aristolochiaceae*, they are very different, as are also the essential oils obtained from them. The oil from *A. Europæum* differs from that from *A. Canadense* in that the former contains the crystalline substance asarone, but apparently none of the alcohols or esters which are present in the latter. With regard to the colour of the oil, the chemical change noted by Kremers in oil of *monarda* would account for the red or brown

colour of certain oils, but the colour of the blue oils must be attributed to substances of a totally different character.

155. "On the Oxidation of Sulphurous Acid to Dithionic Acid by Metallic Oxides." By H. C. H. CARPENTER.

Only two metallic oxides have hitherto been found to react with sulphurous acid so as to produce dithionic acid. These oxides are manganese dioxide and hydrated ferric oxide.

The object of the present research was the investigation of reactions which lead to the formation of dithionic acid, particular care being taken as to the purity of the sulphurous acid and the various oxides used. Dithionic acid is obtained when sulphurous acid reacts with (a) hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, entirely freed from manganese; (b) hydrated manganic oxide, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and (c) hydrated cobaltic oxide, $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, but not with hydrated nickelic oxide, $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

With hydrated ferric oxide, an almost theoretical yield of dithionic acid is obtained. Although it has not been found possible to obtain the theoretical yield of this acid from the corresponding hydrated oxides of manganese, cobalt, or nickel, yet there is very strong reason for believing, on account of the greater development of energy in the reduction of these oxides, that a partial or even complete decomposition of dithionic acid into sulphuric and sulphurous acids would take place. The facts which point to this conclusion are contained in the two following tables. The first shows the percentages of dithionic and sulphuric acids obtained from the four hydrated oxides already mentioned; the second indicates the changes of energy, expressed in thermal units, involved in the reduction of the oxides.

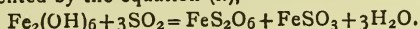
I.

Hydrated oxides.	Percentage dithionic.	Percentage sulphate.
Ferric	96.06; 96.23	Not estimated
Manganic	75.52; 74.53	25.42
Cobaltic.. ..	36.97; 35.07	63.80; 63.33
Nickelic.. ..	Nil	101.04

II.

Reduction of the hydrated oxides.	Heat of reaction.
$\text{Fe}_2(\text{OH})_6 = 2\text{Fe}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	-546 K
$\text{Mn}_2(\text{OH})_6 = 2\text{Mn}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	-448 K
$\text{Co}_2(\text{OH})_6 = 2\text{Co}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	-225 K
$\text{Ni}_2(\text{OH})_6 = 2\text{Ni}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} \dots$	+ 13 K

A comparison of the two tables shows that the greater the energy required for the reduction of the hydrated oxides, the larger is the percentage yield of dithionic acid. The maximum yield is obtained with ferric hydrate, where the energy that needs to be supplied is such that it is possible to stop the reaction almost wholly at the stage represented by the equation (i.),—



Whether the slight deficit from the theoretical number is due to a slight decomposition of the nature (ii.), $\text{Fe}_2\text{O}_6 = \text{FeSO}_4 + \text{SO}_2$, or to a defect in the method of estimation used, is a question which it has not been found possible to decide.

In the case of manganic oxide about one-quarter, and in the case of cobaltic oxide about two-thirds, of the dithionic acid formed is decomposed in the manner indicated in equation (ii.).

The reduction of nickelic oxide differs essentially from that of the other three in being an exothermic change, and the energy liberated is such that the reaction cannot be stopped at the intermediate stage, but proceeds wholly to the last stage, and the only oxidation product is sulphuric acid.

The author has confirmed the results of Gay-Lussac and Welter, who showed that no dithionic acid was obtained by the reduction of the peroxides of lead and barium with sulphurous acid. In view of the negative character of these results, the action of sulphurous acid on the dithionates of these metals was studied. It was found that solutions of barium dithionate are quite unaltered,

except at a temperature at which the influence of heat alone begins to be seen, when a gradual decomposition into barium sulphate and sulphur dioxide sets in. On the other hand, solutions of lead dithionate are decomposed instantaneously, even at 5°, lead sulphite being precipitated, and free dithionic acid remaining dissolved.

156. "Optically Active β Hydroxybutyric Acids." (Preliminary note). By A. MCKENZIE.

For certain work the author has been desirous of obtaining *d*- and *l*-hydroxybutyric acids. That a substance so simply constituted as externally compensated β -hydroxybutyric acid has not before this been resolved into its optically active components is due to the fact that the salts formed by neutralisation with the common alkaloids are readily soluble and crystallise with some difficulty. The author has resolved the inactive acid, which was prepared by the reduction of acetoacetic ester by sodium amalgam, by means of quinine with water as solvent. After systematic crystallisation, the neutral *l*-acid-*l*-quinine salt was isolated. This salt, which crystallises well, contains $4\frac{1}{2}\text{H}_2\text{O}$, is very easily soluble in cold ethyl alcohol, moderately so in chloroform, sparingly so in benzene, acetone, carbon tetrachloride, and in ether, and easily in boiling ethyl acetate. An alcoholic solution of the air-dried salt had the rotation $[\alpha]_D^{15} = -129.9^\circ$ ($c=2.814$). The anhydrous salt melted at $124.5^\circ\text{--}125.5^\circ$. The *l*-acid from the quinine salt gave $[\alpha]_D^{16} = -24.9^\circ$ ($c=8.3304$), whilst the sodium salt prepared from it gave $[\alpha]_D^{15} = -14.5^\circ$ ($c=8.518$). These values for the specific rotations of the acid and its sodium salt agree with the values of Magnus-Levy, who obtained the *l*-acid from diabetic urine (*Archiv. für Experim. Path. und Pharmac.*, 1901, xlv., 389).

The author prepared some *l*-acid from diabetic urine by the method of Magnus-Levy, and converted it into quinine salt. The product, when deprived of its water of crystallisation, melted at $124.5^\circ\text{--}125.5^\circ$; an alcoholic solution of the air-dried salt gave $[\alpha]_D^{15} = -129.9^\circ$ ($c=2.8052$).

Experiments are in progress with the object of isolating the *d*-acid by means of strychnine, the *d*-acid-*l*-strychnine salt being more insoluble in water than the *l*-acid-*l*-strychnine salt.

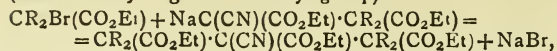
157. "Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide." By J. B. COHEN and H. D. DAKIN.

By the reduction of 1 : 3 : 5-trinitrobenzene and 2 : 4 : 6-trinitrotoluene in alcoholic solution with hydrogen sulphide in presence of a trace of ammonia, the corresponding dinitrohydroxylamine compounds are formed, $\text{C}_6\text{H}_3(\text{NO}_2)_3 + 2\text{H}_2\text{O} = \text{C}_6\text{H}_3(\text{NO}_2)_2\text{NHOH} + \text{H}_2\text{O}$. *Dinitrophenylhydroxylamine* is an orange, crystalline substance, m. p. $114^\circ\text{--}116^\circ$, soluble in alcohol, benzene, and in hot dilute hydrochloric acid; *dinitrotolylhydroxylamine* crystallises from benzene in yellow rhombohedral crystals, and from dilute hydrochloric acid in needles, m. p. $143^\circ\text{--}145^\circ$. Both compounds reduce alcoholic silver nitrate and Fehling's solution; they are slowly decomposed on boiling with dilute, more rapidly with concentrated hydrochloric acid, yielding the amido compounds, and losing oxygen, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NHOH} = \text{C}_6\text{H}_3(\text{NO}_2)_2\text{NH}_2 + \text{O}$. In the case of trinitrotoluene, the nitro-group in the ortho-position undergoes reduction, a curious fact, seeing that ammonium sulphide effects the reduction of the para-nitro-group. The 2 : 4-dinitro-6-toluidine, obtained by the action of strong hydrochloric acid on dinitrotolylhydroxylamine, is a colourless substance, crystallising in needles, and melting at $212^\circ\text{--}213^\circ$.

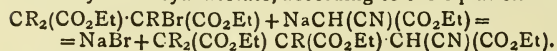
158. "The Synthesis of Alkyl-substituted Tricarballic Acids." By W. A. BONE and C. H. G. SPRANKLING.

The authors have investigated two methods for the preparation of ethyl cyanotricarballicates from succinic acids, as follows;—(i) By the interaction of the sodium compounds of ethyl cyanosuccinates with the esters of

α -bromo-fatty acids, as indicated by the general equation (where R=hydrogen or an alkyl group) —



and (2) by the interaction of ethyl monobromosuccinates with ethyl sodiocyanacetate, according to the equation —



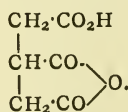
They find that whilst the first method is quite a general one, and affords good yields of ethylcyanotricarballylates, the second has a more limited application (mainly on account of the tendency which ethyl bromosuccinates exhibit to lose hydrogen bromide, and form unsaturated esters), and even in cases where it can be applied, the yields are not so good as those obtained by the first method. The properties of tricarballylic acid itself, and a number of alkyl-substituted acids of the series, their anhydro-acids, and monomethyl salts have been studied. Some of these are indicated in the following table:—

Acid.	M. p.	Dis- sociation constant.	M. p. of anhydro- acid.
Tricarballic	157—159	0.022	130—131
α -Methyltricarballylic ..	(1) 179	0.0322	liquid
	(2) 134—135	0.0480	liquid
$\alpha\alpha_1$ -Dimethyltricarballylic	(1) 206—207	0.0450	110—112
	(2) 174	0.0545	130
	(3) 143	0.0572	116—117
$\alpha\alpha$ -Dimethyltricarballylic	143	0.0318	135—136
$\alpha\alpha_1$ -Diisopropyl	(1) 173	0.1930	liquid
	(2) 156	0.1625	liquid

Monomethyl salts of tricarballylic and $\alpha\alpha$ -dimethyltricarballylic acids have been prepared by three methods, namely, (1) direct partial esterification of the acids, (2) partial hydrolysis of trimethyl salts, (3) the solution of anhydro-acids in methyl alcohol. The products are liquid, but a study of their dissociation constants shows that each of the three methods indicated yields a *single* monomethyl salt, and not a mixture of isomeric monomethyl salts. The dissociation constants of these salts are as follows:—

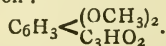
Acid.	Monomethyl salts by		
	Direct esterifica- tion of acid	Partial hydrolysis of trimethyl salt	Solution of anhydro- acid in CH_3OH .
Tricarballic	0.0075	0.00925	0.00945
$\alpha\alpha$ -Dimethyltricarballylic	0.0180	0.00865	0.0186

Since the monomethyl salts obtained by direct esterification of the acids most probably have the formulæ $\text{CH}_2(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2(\text{CO}_2\text{Me})$ and $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2(\text{CO}_2\text{Me})$ respectively (because a carboxyl attached to a *primary* carbon atom is always more readily esterified than one attached to a secondary or tertiary carbon), it follows that the monomethyl tricarballylate obtained by partial hydrolysis of the trimethyl salt, and by solution of the anhydro-acid in methyl alcohol, must have the formula $\text{CH}_2(\text{CO}_2\text{H}) \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2(\text{CO}_2\text{H})$, and therefore that the constitution of the anhydro-acid must be represented thus,—



159. "Note on the Constitution of Limettin." By W. A. TILDEN and H. BURROWS.

In a previous communication (Tilden, *Trans.*, 1892, lxi., 344), it was shown that limettin, $\text{C}_{11}\text{H}_{10}\text{O}_4$, had the following composition:—



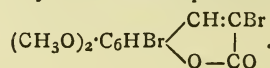
Further experiments have been undertaken with the object of determining the structure of the group C_3HO_2 .

In the meantime, the publication of a communication by E. Schmidt (*Apoth. Zeit.*, 1901, lxxi., 619) on a substance which he has isolated from oil of lemon, and has identified with limettin, and the appearance of a recent note by Burgess (*Proc.*, 1901, p. 171) render it necessary to place on record the following results, although at present incomplete.

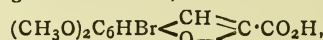
The dibromo-compound previously described by Tilden (*loc. cit.*) melts at 297° with decomposition, and not at 257° .

On treatment with 10 per cent solution of potash, it yields an acid of the composition $\text{C}_{11}\text{H}_9\text{O}_5\text{Br}$. Continued treatment with potash does not remove the second atom of bromine.

It is therefore highly probable that the structure of the group C_3HO_2 is similar to that of the ring in coumarin, dibromocoumarin behaving in exactly the same way. Dibromolimettin may therefore be represented as—



When treated with potash, dibromolimettin gives the corresponding coumarilic acid,—



from the potassium salt of which the methyl ester was prepared (m. p. 181°).

On subjecting dibromolimettin to further action of bromine in a sealed tube, a tribromo-derivative was prepared containing two hydroxyl groups; the corresponding diacetyl compound melts at 244° .

The following chlorine compounds have been prepared:—

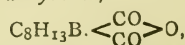
Monochlorolimettin, which melts at 242° and is not acted upon by solutions of alkaline hydroxides. *Dichlorolimettin* melts at 275° and, like the dibromo-compound, with potash gives *monochlorocoumarilic acid*. The trichloro-derivative prepared by Tilden (*loc. cit.*) similarly gives *dichlorocoumarilic acid*.

When limettin is heated on the water-bath with a solution of sodium ethoxide, the sodium salt is quickly deposited. Attempts to prepare the methyl derivative were unsuccessful, but when the silver salt was heated with a solution of methyl iodide in methyl alcohol, a substance which crystallised in white tufts of needles (m. p. 189°) was isolated, together with re-formed limettin. Analyses showed the substance to have the formula $\text{C}_{12}\text{H}_{12}\text{O}_4$, differing from limettin by CH_2 . Its chemical properties are similar to those of limettin, as it readily forms a bromo-derivative and a coumarilic acid.

160. "Derivatives of β Bromocamphor." By H. E. ARMSTRONG and T. M. LOWRY, D.Sc.

By heating ordinary $\alpha\alpha'$ -dibromocamphor with hydrogen bromide under certain conditions, it is converted into an isomeric $\alpha\beta$ -compound, one of the bromine atoms being transferred from the lateral CBr_2 group. Kachler and Spitzer have shown that this $\alpha\beta$ -dibromocamphor is converted by nitric acid into an $\alpha\beta$ -dibromonitrocarnphor. The authors find that a β -bromocamphoric acid is also produced, isomeric with the acids described by Wreden and by Kipping and Pope. The close resemblance between this β -acid and the isomeric π -acid suggests that the two compounds are similar in constitution—perhaps stereoisomerides; in other words, that the bromine is present in one of the median methyl groups in the $-\text{CMe}_2-$ group of the camphor molecule.

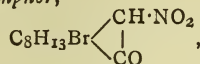
β -Bromocamphoric acid, $\text{C}_8\text{H}_{13}\text{Br}(\text{CO}_2\text{H})_2$, softens at about 205° and melts at $208-210^\circ$, gas being liberated; in a 5 per cent solution in alcohol at 10° , $[\alpha]_D = +39.7^\circ$. The corresponding anhydride,—



crystallises from dilute acetone in long glistening needles;

t melts at 142° ; in a 4 per cent solution in acetone at 10° , $[\alpha]_D = -2.8^{\circ}$.

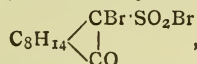
β -Bromonitrocarnphor,—



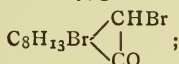
prepared by reducing $\alpha\beta$ -dibromonitrocarnphor, crystallises from alcohol in short prisms; when heated, it softens at 100° and melts at 112° , but after fusion and solidification re-melts sharply at 100° ; being a secondary nitro-compound, it forms salts; and freshly-prepared solutions exhibit the phenomena of mutarotation.

A third product of the action of nitric acid on $\alpha\beta$ -dibromocarnphor is a *tribromocarnphor*, $\text{C}_{10}\text{H}_{13}\text{Br}_3\text{O}$, which melts at 66° ; in a 2.5 per cent solution in acetone, $[\alpha]_D = +2^{\circ}$; it separates in a crystalline form on reducing the crude crystalline dibromonitrocarnphor, and appears to be identical with the compound obtained by de la Royère by heating $\alpha\beta$ -dibromocarnphor with phosphorus pentabromide (*Bull. Soc. Chim.*, 1882, xxxviii., 580).

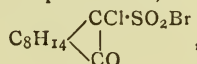
β -Bromo-derivatives of camphor are also obtained on decomposing by heat the sulphobromides derived from the "Reychler" series of acids (Armstrong and Lowry, *Proc.*, 1901, p. 182); e.g., α -bromocarnphor- α' -sulphobromide,—



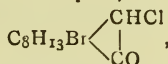
when decomposed in this way, gives $\alpha\beta$ -dibromocarnphor,—



α -chlorocarnphor- α' -sulphobromide,—



gives α -chloro- β -bromocarnphor,—



the products obtained being identical with those formed by heating α -bromocarnphor and α -chlorocarnphor with bromine in sealed tubes.

THE INSTITUTE OF CHEMISTRY.

ON Wednesday evening last, the 4th of December, the Annual Dinner of the Fellows and Associates of the Institute of Chemistry was held in the Whitehall Rooms at the Hotel Metropole. The chair was taken by Professor J. Millar Thomson, LL.D., F.R.S.; the guests numbering about 150. Among those present were Lord Monkswell, Lord Reay, Mr. Hanbury, M.P., the Hon. W. P. Reeves, Professor Rücker, Sir James Crichton Browne, Professor Ramsay, Mr. C. Hawksley, Mr. H. G. Howes, &c.

After the usual toasts of the King, the Queen, and the rest of the Royal Family had been duly honoured, Mr. A. GORDON SALAMON proposed the "United Forces," and he took occasion to point out how dependent those forces are upon chemists, both for "quick killing" and food supply in time of war. This toast was responded to by Colonel J. JOCELYN, R.A.

Prof. RAMSAY then proposed "The Houses of Parliament" in a very able speech. He first referred to the recent Jubilee of Professor Berthelot in Paris, and laid great stress on the manner in which the French Government had co-operated with the scientific societies to honour this great chemist; he regretted that although the English Government take the advice of the most capable of the scientific men in England on various important points, such as explosives, surgery in warfare, the adulteration of food and drugs, &c., they do not as a rule honour science

generally in the persons of those who have most distinguished themselves, as is done abroad. After referring to the importance of the Institute of Chemistry and the value of the degree F.I.C., he touched on the question of the chemistry of water supplies, and gave it as his opinion that, valuable as the bacteriological examination of water may be, it merely confirmed the views of the chemist. He regretted that more chemists are not employed on the Geological Survey, as in the United States, and eulogised the work done by the inspectors under the Alkali Act.

This toast was responded to by Lord MONKSWELL in an amusing speech, in which he pointed out the manifold advantages of being a member of the House of Lords.

Mr. HANBURY replied for the House of Commons, and he admitted that Government does not always honour science as it should do; he referred to some of the great discoveries which had been made in this country, such as that of aniline dyes, the manufacture of which had gone to Germany, and suggested that salaries were, as a rule, too low in England. Government, he thought, owed a great deal to scientific men, though so few of them had been members of the Privy Council. Agriculture especially was greatly in debt to the chemist, and he thought that no profession required so much all-round knowledge as that of agriculture. He thought, however, that if science could be tempered with practice, and the "hideous terminology," which frightened farmers, done away with, it would be for the ultimate benefit of the country at large. He pointed out the great importance of the discovery of the nodules on leguminous plants which have the faculty of fixing nitrogen from the air, and hoped that further similar discoveries would be made in other branches of agriculture. In this connection he referred to the valuable results obtained by the exporters of butter from Australia, who were now, thanks to a microbe, enabled to land their butter in England in as good condition as that imported from Denmark.

Lord REAY then proposed the "Institute of Chemistry," which toast was ably responded to by the PRESIDENT, who, after referring to the work of the Educational Department, pointed out the importance of the Institute of Chemistry, which though comparatively young had a member-roll of 1040 members, 150 registered students, with 40 more coming up for examination in January next. He urged the necessity of keeping up the high standard of qualifications, combined with the high sense of professional responsibility.

Prof. WM. TILDEN gave "Prosperity to Science and to Scientific Industries," and was proud of the position taken by British men of science. This toast was responded to by Prof. RÜCKER, who advocated the union of pure and industrial science, which when united will stand, but when divided may fall. Mr. CHARLES HAWKSLEY also responded to this toast, referring specially to recent work done on the purification of sewage.

The last toast was the "Visitors," proposed by Mr. FRISWELL, and responded to by Mr. H. G. HOWSE, President of the Royal College of Surgeons.

The Dehydration of Selenite and the Hydration of Anhydrite.—V. Zunino.—While working with artificial gypsum the author found that the dehydration was complete at 188° . After heating to 230° the product re-absorbs all its water of crystallisation in the presence of steam; if heated to 280° it no longer does so. By melting together a mixture of CaSO_4 and NaCl for a few hours, and then letting it cool slowly, he obtained, after levigation, trimetric crystals of anhydrite. It is also possible to obtain this body in small quantities by boiling gypsum for about six hours with a saturated solution of common salt. This anhydrite re-absorbs water, and becomes transformed into gypsum after prolonged contact with water.—*Gazz. Chim. Ital.*, [1], vol. xxx., p. 333.

NOTICES OF BOOKS.

Prospecting for Gold. A Handbook of Practical Information and Hints for Prospectors based on Personal Experience. By DANIEL J. RANKIN, F.R.S.G.S., M.R.A.S. With Illustrations specially Drawn and Engraved for the Work. London: Crosby Lockwood and Son. 1901. Pp. 184.

PROSPECTING for gold has nearly always been carried on in the most haphazard manner by men who worked simply by "rule-of-thumb," or by no rule at all.

A rumour comes down to camp that some one has struck gold away up country, and there is immediately a rush; most of the men know nothing about geology, mineralogy, or mining, but they go on "spec," and sometimes the good thing "comes off," but more often the expedition ends in failure.

The aim of the compiler of this handbook has been to furnish the "intelligent" prospector with information—in a portable form—for which hitherto he would have had to refer to a number of larger volumes. Among the authorities drawn upon we may mention such well-known names as J. D. Dana, Mr. Warnford Lock, Mr. Landauer, Mr. J. A. Miller, &c.

After describing the principal kinds of rocks, the author proceeds to a consideration of their structure, condition, and arrangement, and gives a list of the minerals associated with gold; while special attention is paid to gold in South Africa, and the banket formation.

Methods for the preliminary determination of gold in quartz and ores are given, as well as detailed information with regard to prospecting for alluvial gold, and for auriferous veins and rocks.

It is well known amongst mining men that some of the best paying gold mines are those in which the gold is so finely divided as to be practically never visible in the ores; the prospector should bear this in mind, and not be led away by a few rich specimens, which may possibly contain all the gold for many yards round.

Chapter VIII. is an important one, and contains a large number of tables showing the characteristics of all the principal ores, not only of gold, but of other metals that may be met with, as well as instructions for their preliminary analysis, and special tests. A pocket at the end of the book contains a very useful table, which has been compiled to furnish the prospector with a ready, comprehensive, and clear view of all those characteristics of the mineral ores associated with gold that might facilitate their recognition *in situ*.

This volume is the best we have met with of its kind, and cannot fail to be of service to those for whom it was specially intended.

The Extra Pharmacopœia. By WILLIAM MARTINDALE, F.L.S., F.C.S., and W. WYNN WESTCOTT, M.B.Lond., D.P.H. Tenth Edition. London: H. K. Lewis, 1901. Pp. 688.

SINCE the publication of the last British Pharmacopœia a new edition of the Pharmacopœia Germanica has been published; an Indian and Colonial addendum to the British Pharmacopœia, 1898, and a supplement to the Austrian Pharmacopœia, as well as a revision of the Formulary of the British Pharmaceutical Conference, have also been issued. In preparing this—the tenth edition—the authors have carefully studied all these from the pharmaceutical point of view, as well as noting the current literature, so that they may now be said to present a fair review of the condition of pharmacy and therapeutics at the present time.

Synthetic compounds continue to be in demand, but the chemical products of vegetable origin have not attracted much attention, with the exception of certain morphine derivatives and pilocarpine salts.

Among anæsthetics, ethyl chloride has been found of service, especially by dentists. Bromopin and iodopin have been recommended as nerve sedatives; while peroxide of hydrogen has met with some favour as a germicide in France and America.

Besides these few substances which catch our eye there are, of course, a large number of new remedies which cannot be specially mentioned here; we may, however, add that the whole work has been most carefully prepared, and is worthy of its authors.

Twenty-fifth Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the Year 1900. London: Eyre and Spottiswoode. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1901. Pp. 209.

THE only modification of the law made during the past year concerning explosives has been an Order in Council in regard to acetylene gas when in admixture with oxygen or air. The full text of the Order will be found in Appendix F, p. 76.

The growth of trade in explosives has continued at an increased rate; this is shown by the greater increase in the number of factories as well as by their increased activity.

The result of 217 visits of inspection show that in the great majority of cases the conditions and management are excellent, and that there has been no falling off in the high standard previously attained. It is, however, to be regretted that at many places the supervision of registered premises by the Local Authority leaves much to be desired.

The number of deaths by accident in manufacture (9) is unfortunately double the average for the decade (4.5), but even this is a low death-rate as compared with that in many other trades.

The number of factories under continuing certificate or licence is 150, but this does not include "toy firework" or "small firework" factories. Four factories have become extinct during the year, while three new ones have been established, and eleven more applications are under consideration.

The total number of persons employed in factories under the Act shows a steady increase as follows:—

Year	1885	1890	1895	1900
No. of persons..	7484	9820	10,023	11,098

It will be seen, in Dr. Dupré's report, that out of 339 samples examined by him, 50 were rejected.

The number of accidents during the year is 77, causing 9 deaths, and injuries to 35 persons; most of these, however, were unimportant, and the injuries sustained slight.

The total number of licensed magazines is now 385, being a decrease of 7; but this decrease is only nominal, being caused by the absorption into factory 156 (Kent) of the 7 magazines owned by the Thames Storage Company.

There has been no modification of the law in regard to the packing of explosives during the year.

There has been a slight rise in the amount of explosives imported during the year, but it is again pointed out that a considerable amount of this is not for home consumption, but is simply brought into this country for re-shipment abroad, and each transaction must be covered by an importation licence, and every cargo sampled and examined, exactly as if it were for home consumption.

Though there are no statutory powers in respect of carbide of calcium or acetylene, except when the latter is in a condition which brings it under the Explosives Act, yet the inspectors are frequently consulted on questions connected with both substances, and, at the request of the Board of Trade, they have prepared a Model Code of Harbour By-laws for carbide of calcium for the assistance of harbour authorities. This code is to be found in Appendix Y, p. 195.

Leitfaden für den Unterricht in der Anorganischen Chemie.

By Dr. J. SPERBER. Erster und Zweiter Teile. Zürich:
E. Speidel.

THESE two volumes, which comprise the first and second parts of a "Guide to the Study of Inorganic Chemistry," to be followed by a third part, deal with the non-metals and their most important compounds with one another. The book does not claim to be an exhaustive treatise, but it would be hard to find compressed into such small compass more complete and comprehensive accounts of the preparations, properties, and reactions of the various substances treated of. The author's style throughout is concise, clear, and graphic; and the illustrations, which are plentiful, are particularly good. One special feature of the book is the attention paid to structural formulæ, the grounds for which are fully explained; as, for instance, in the case of sulphurous acid. Such explanations, if thoroughly assimilated, will probably very materially simplify for the student the study of organic chemistry. Another point on which the author is to be complimented is the introduction of short explanations and discussions of such theoretical subjects as thermochemical phenomena, dissociation, &c., at appropriate places in the text as suitable examples are met with in illustration of them; such an arrangement tends both to emphasise the facts concerned and to simplify the theory, and is greatly preferable to the more usual method of prefacing the detailed study of the elements with a purely theoretical introduction.

In the second volume, which deals with the oxygen compounds of the metalloids, considerable space is devoted to the commercial process for the manufacture of sulphuric acid; the most recent investigations on the reactions of the chamber gases are fully explained, and an ingenious diagram is given to illustrate the various processes probably occurring in the lead chambers.

The absence of any reference to the periodic system is to be regretted, inasmuch as the law of periodicity serves to throw light upon the relations of the elements of each group among themselves, and of the various groups to one another.

Meeting called, after a fortnight's notice, to specially consider the subject.

The object of the meeting on Thursday is practically to protest against the decision of the Council, which is in direct opposition to the wishes of the Society, as expressed at the Extraordinary General Meeting.—I am, &c.,

FREDERIC JAS. M. PAGE.

Chemical Laboratory, London Hospital,
December 11, 1901.

FLAME COLOURATION OF NICKEL.

To the Editor of the Chemical News.

SIR,—In a recent report of the transactions of the Chemical Section of the British Association Meeting at Glasgow in September last, I read:—Mr. P. J. Hartog, in describing "The Flame Colouration and Spectrum of the Nickel Compounds," said that nickel acetate produced an evanescent purple tinge, and a persistent red colouration in the Bunsen flame. Professor Smithells remarked that, although experiments with nickel had been made for years, this property had not been observed, and the colouration perhaps might not be due to nickel.

The writer made the same observations in regard to the flame colourations of nickel salts in 1897, and the whole matter was fully discussed in a paper by Professor T. W. Richards and the writer entitled "A Revision of the Atomic Weight of Nickel." This paper was reprinted in the *CHEMICAL NEWS* (vol. lxxiv., p. 286 *et seq.*).

Gerhardt Krüss noticed a rose-coloured flame in connection with certain nickel compounds as far back as 1889, and believed that it was caused by the presence of an unknown element.

Professor Smithells was therefore mistaken in saying that this property of certain nickel compounds had never been observed.—I am, &c.,

ALLERTON CUSHMAN.

1526, New Hampshire Avenue,
Washington, D.C., November 18, 1901.

CORRESPONDENCE.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—The letter which you published on December 6th (*CHEMICAL NEWS*, vol. lxxiv., p. 278) from an anonymous "Fellow of the Chemical Society" on the proposed alteration of the meetings of the Society from 8 on Thursday to 5.30 on Wednesday, does not give an accurate idea of the present state of the case. It is true that a post-card vote gave 188 votes in favour of and 78 votes against the change, but I do not believe this vote expressed the real feeling of the Society in the matter. The post-card vote was sprung upon us without any warning, and we were asked to tend our vote without delay; several who signed in favour of the change have since altered their opinion. Many thought the change would be against the best interests of the Society, and so a special meeting was summoned by the President to discuss the question; due notice of this meeting was given, and, as far as I know, it was a representative meeting of those Fellows who regularly attend; at all events it was open to everyone who was interested in the question and who chose to take the trouble to be present. Nothing practically was said in favour of the change, and much against it, and as a result, by an almost unanimous vote (99 to 5), it was decided that the change was undesirable.

No one will surely contend that a hastily-taken post-card plebiscite can have any weight when compared with a deliberate and almost unanimous vote taken at a Special

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

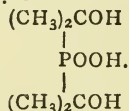
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 21, November 18, 1901.

Ammonium Amalgam.—Henri Moissan.—Various chemists have proved the existence of a so-called ammonium amalgam without precisely determining its composition. This amalgam was obtained by acting with pasty sodium amalgam on a saturated solution of ammonium chloride, and the reaction was represented by the equation $\text{NH}_4\text{Cl} + \text{Na}, n\text{Hg} = \text{NH}_4, n\text{Hg} + \text{NaCl}$; the exact value of n never having been determined. The author now finds, in a series of preliminary experiments, that if a solution of the chloride or iodide of ammonium in anhydrous ammonia acts on sodium amalgam, a metallic mass is obtained, in which the hydrogen and ammonia are apparently present in stable combination at a temperature of -39° . This metallic mass, when undergoing decomposition at ordinary temperatures in the absence of water, increases to thirty times its volume and evolves two volumes of ammonia gas for one volume of hydrogen.

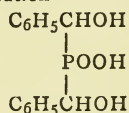
Compounds of Gold with Chlorine.—Fernand Meyer.—The author's experiments on the possibility of a total transformation of a given quantity of gold into crystallised auric chloride by chlorine, lead him to the conclusion that this transformation can only be accomplished by the action of liquid chlorine, owing to the difference in the solubility of the chloride in cold or hot chlorine.

When thus obtained, the auric chloride is in the form of beautiful crystals. A study of the dissociation of this liquid chloride enables the author to discover the conditions of temperature and pressure which must be used in order to obtain AuCl_3 or AuCl . It also shows that a single less chlorinated compound of gold than AuCl_3 exists, and this is AuCl . He intends to continue this research to the other halogen compounds of gold.

Dioxyisopropylhypophosphorous Acid.—C. Marie.—The formulæ of the salts and ethers of dioxyisopropylhypophosphorous acid show that it is monobasic, and similar to hypophosphorous acid from which it is derived; also, the existence of diacetyl and dibenzoyl derivatives lead the author to believe that two oxyhydriles are present in this acid, and he therefore believes it to possess the following constitution:—



Such a body is then the analogue of the dioxybenzylphosphinic acid obtained by M. Ville (*Comptes Rendus*, cviii., p. 659) by the action of aqueous hypophosphorous acid on benzoic aldehyde, and which, from its properties, ought to possess the constitution—



Action of certain Acid Chlorides on Methyl and Ethyl Sodacetylacetates.—M. Bongert.—In a preceding paper in collaboration with M. Bouveault, the author described his researches on the action of butyryl chloride on methyl sodacetylacetate. He now uses a more general reaction by employing, not only other acid chlorides, but also a different ketonic ether.

Oxidation of Non-saturated Alcohols by the Action of Contact. Preparation of Vanilline.—A. Trillat.—The action of catalytic phenomena, provoked by contact, of certain porous substances at a high temperature can be generalised to non-saturated alcohols of the fatty and also of the aromatic series. Under the influence of the porous material there appears to be a rupture of the molecule, with formation of an aldehyde. Oxidation is even energetic enough to maintain the body in contact in a state of incandescence, as in the case of allylic alcohol. The partial transformation of isoeugenol into vanilline was a particularly interesting result of this investigation.

MISCELLANEOUS.

Subject-matter Index of Mining and Metallurgy.—The Council of the North of England Institute of Mining and Mechanical Engineers will publish shortly a Subject-matter Index of Mining and Metallurgical Literature for the year 1900, and will thereafter continue it yearly. It is expected that it will form a volume of 200 pages, comprising entries of about 8000 separate papers published during the year.

Nitrohydroxylamic Acid.—A. Angeli and F. Angelico.—The salts of this acid were obtained from the sodic salt; viz., the potassium salt $\text{K}_2\text{N}_2\text{O}_3$; the calcium salt $\text{CaN}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (dried at 125°), the strontium salt with $\frac{1}{2}\text{H}_2\text{O}$ (dried at 110°), and the anhydrous lead salt. Acids decompose these salts quantitatively according to the equation $\text{H}_2\text{N}_2\text{O}_3 = 2\text{NO} + \text{H}_2\text{O}$. To split it up into nitrous acid and protoxide of nitrogen it suffices to boil the aqueous solution of the soda salt, $2\text{Na}_2\text{N}_2\text{O}_3 = 2\text{NO}_2\text{Na} + \text{N}_2\text{O} + \text{Na}_2\text{O}$. To split it up into hyponitrous acid and nitrous acid it suffices to melt the sodium salt, $2\text{N}_2\text{O}_3\text{Na}_2 = 2\text{NaNO}_2 + \text{N}_2\text{O}_2\text{Na}_2$.

If we treat an aqueous solution of the sodium salt with an aldehyde, the monomolecular hyponitrous acid, HON , which is formed, unites with the aldehyde, giving a hydroxylamic acid. For example, $\text{CH}_3\text{COH} + \text{NOH} = \text{CH}_3\text{—C} \begin{smallmatrix} \text{NOH} \\ \text{OH} \end{smallmatrix}$. —Gazz. Chim. Ital., [1], vol. xxx., p. 593.

Some Reactions of Hydration.—P. Roland.—The author has examined the retarding (or otherwise) action of a number of salts on the solidification of lime, Portland cement, and plaster. The following table gives his results:—

	Lime or Portland cement.	Plaster.
Chloride of sodium	No action	Accelerated
“ lithium	Accelerated	“
“ calcium	“	No action
“ aluminium	“	Accelerated
Bichromate of potassium or chromate of calcium ..	Retarded	“
Boric acid or borax	“	Retarded
Carbonate of sodium	Accelerated	“
Sulphate of potassium ..	Retarded	Accelerated

—Berichte, xxxiii., p. 2831.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). “The Chemistry of Confectioners’ Materials and Processes,” by W. Jago, F.C.S., F.I.C.

WEDNESDAY, 18th.—Society of Arts, 8. “Range Finders,” by Prof. George Forbes, F.R.S.

Microscopical, 7.30. An Exhibition on “Development and Structure of Eyes” (illustrated by Micro-slides), by F. W. Watson Baker.

THURSDAY, 19th.—Chemical, 8. “Corydaline—Part VII., The Constitution of Corydaline” and “The Relation of Corydaline to Berberine—The Oxidation of Berberine with Nitric Acid,” by J. J. Dobbie and A. Lauder. “The Magnetic Rotation of some Polyhydric Alcohols, Hexoses, and Disaccharoses,” by W. H. Perkin, F.R.S. “Stereo-isomeric Halogen Derivatives of α -Benzoylcamphor,” by M. O. Forster and F. M. G. Micklethwait. “Is Argon an Elementary Substance?” by G. Martin.

DR. A. ISBERT, Technical Business,
FRANKFORT-ON-MAIN, GERMANY.

ESTABLISHED 1888.

Undertakes the sole Sale of profitable special articles in the TECHNICAL and CHEMICAL LINES for GERMANY.

GENERAL AGENTS WANTED for the SALE in Great Britain, of our
DISINFECTING AND DRAINAGE SUBSTANCE,

“**PINOL**,”

The preparation is recommended by leading experts and official bodies; amongst others by the Prussian War Office. Only firms possessing capital and with connections among BUILDING and PAINTERS’ Circles, BREWERIES, OFFICIAL BODIES, &c., need apply to the—
DEUTSCHE VERTRIEBS-GESELLSCHAFT “PINOL,”
NÜRNBERG (BAVARIA).

ST. PAUL'S SCHOOL.—An Examination will be held at St. Paul's School, West Kensington, on Tuesday, January 14th, 1902, and following days, for filling up about Four Vacancies on the Foundation.—Full particulars can be obtained from the Bursar.

COVERS FOR BINDING.

Cloth, Gilt-lettered Covers for Binding the Half-yearly Volumes of the

CHEMICAL NEWS

may now be obtained. Price 1s. 6d. each.

Volumes Bound in Cloth Cases, Lettered, and Numbered, at 2s. 6d. per volume.

6 & 7, CREED LANE, LUDGATE HILL, E.C.

THE CHEMICAL NEWS.

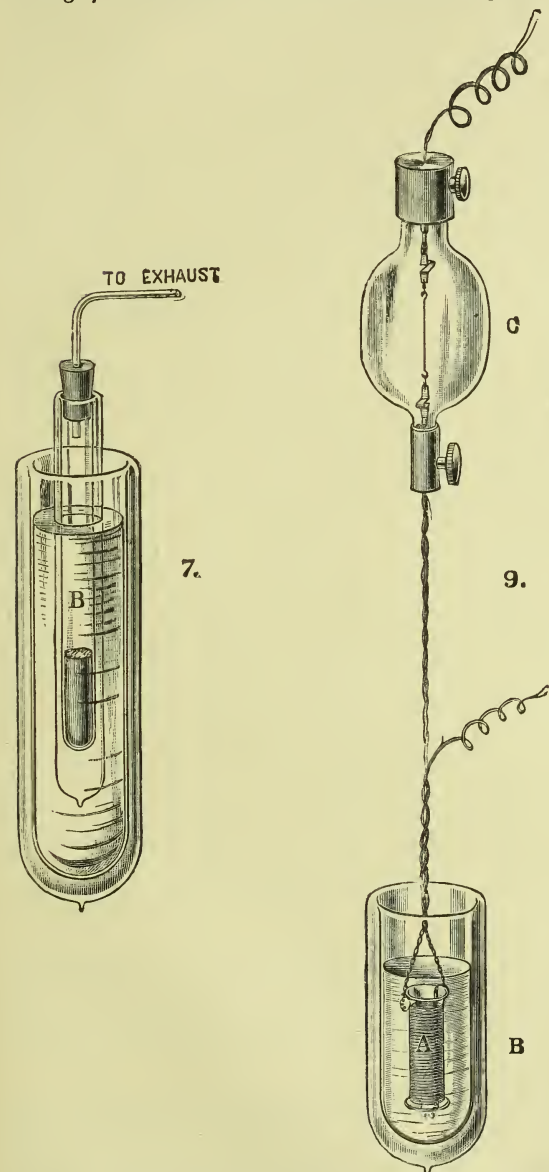
VOL. LXXXIV., No. 2195.

SOLID HYDROGEN.*

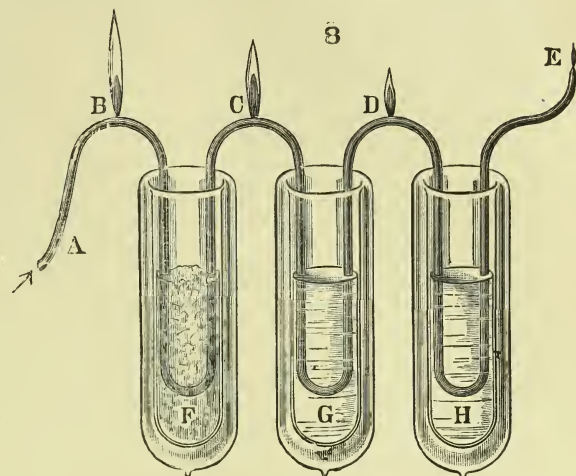
By Professor DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Concluded from p. 282).

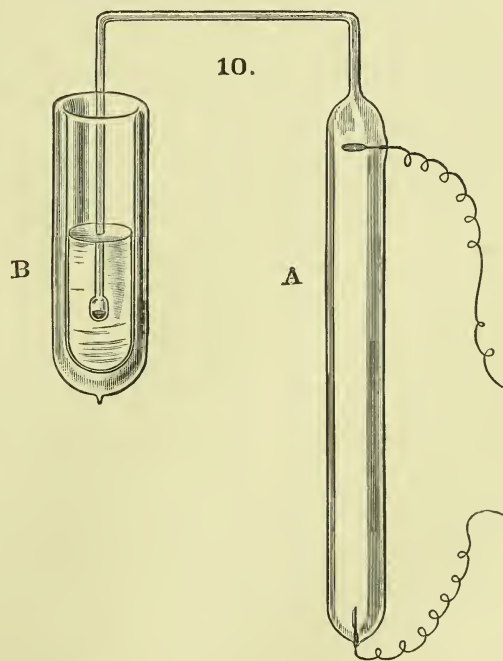
FOR the lecture demonstration of solid hydrogen the apparatus may be most conveniently arranged as is shown in Fig. 7. The small vacuum tube B, after being filled



diminished that it does not exceed that of liquid air in the same vessel when used in the ordinary way. On gradually applying exhaustion to the liquid hydrogen it is forced from its effective heat isolation to pass to a lower temperature, and when the exhaustion reaches 50 m.m. the mass suddenly begins to solidify into a froth-like material.



In order to ascertain the appearance of the hydrogen, made by cooling the liquid produced in a hermetically closed vessel, the following experiment was arranged. A flask of about a litre capacity, to which a long glass tube was sealed, A, B, Fig. 5, was filled with pure dry hydrogen and sealed off. The lower portion B of this tube was cali-



brated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for exhaustion. As soon as the pressure of the boiling hydrogen got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube B, and could be observed accumulating until the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid white

with liquid hydrogen, is immersed in a larger vessel of the same kind filled with liquid air. By this arrangement the rate of the liquid hydrogen evaporation is so much

* A Discourse delivered before the Royal Institution, April 6, 1900.

foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube B when it was covered with a large quantity of this solid, the whole apparatus was turned upside down in order to see whether any liquid would run down from B into the flask A. Liquid did not flow down the tube, so the liquid hydrogen with which the tube was partly filled must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion at about 25 m.m., gradually the hydrogen froth became less opaque, and the solid hydrogen in the tube B was seen to be a transparent ice, but the surface looked frothy. This fact prevented the solid density from being determined, but the maximum fluid density has been approximately ascertained. This was found to be 0.086, the liquid at its boiling-point having the density 0.07. The solid hydrogen melts when the pressure of the saturated vapour reaches about 55 m.m. In order to determine the temperature of solidification two constant volume hydrogen thermometers were used. One at 0° C. contained hydrogen under a pressure of 269.8 m.m., and the other under a pressure of 127 m.m. The mean temperature of the solid was found to be 16° absolute under a pressure of 35 m.m. All the attempts made to get an accurate electric resistance thermometer for such low temperature observations have been so far unsatisfactory. Now that pure helium is definitely proved to be more volatile than hydrogen, this body, after passing through a spiral glass tube immersed in solid hydrogen to separate all other gases, must be compared with the hydrogen thermometer. Taking the boiling-point as 21° absolute under 760 m.m., and the similar value under 35 m.m. is 16° absolute, then the following approximate formula for the vapour tension of liquid hydrogen below one atmosphere is derived:—

$$\log p = 6.7341 - 83.28 / T \text{ m.m.,}$$

where T is the absolute temperature, and p the pressure in m.m. This formula gives for 55 m.m. a temperature of 16.7° absolute. The melting-point of hydrogen must therefore be about 16° or 17° absolute. It has to be noted that the pressure in the constant volume hydrogen thermometer, used to determine the temperature of solid hydrogen boiling under 35 m.m., had been so far reduced that the measurements were made under from one-half to one-fourth the saturation pressure for the temperature. When the same thermometers were used to determine the boiling-point of hydrogen at atmospheric pressure, the internal gas pressure was only reduced to one-thirteenth the saturation pressure for the temperatures. The absolute accuracy of the boiling-points under diminished pressure must be examined in some future paper. The practical limit of temperature we can command by the evaporation of solid hydrogen is from 14° to 15° absolute. In passing it may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting-point is about half the critical temperature. The melting-point of nitrogen is also about half its critical temperature. The foam-like appearance of the solid when produced in an ordinary vacuum vessel is due to the small density of the liquid, and the fact that rapid ebullition is substantially taking place in the whole mass of liquid. The last doubt as to the possibility of solid hydrogen having a metallic character has been removed, and for the future, hydrogen must be classed among the non-metallic elements.

All solid bodies by themselves make very unsatisfactory cooling agents unless we can use them to cool some liquid. Now, with solid hydrogen we can cool no liquid other than hydrogen, so that, for effective cooling, we must use the liquid just above its freezing-point, which is about 16°. It will, however, take a long time to exhaust the wide field of investigation which the use of liquid hydrogen opens up; so we may proceed to illustrate some of its further applications. In former lectures the relation of

electrical resistance to temperature has been discussed, and it was experimentally demonstrated that the curves of resistance of the pure metals all pointed to this quality disappearing or becoming exceedingly small at the absolute zero. This fact has been confirmed, even with the most highly conducting metals, down to the lowest temperature we can command. The experiment illustrated in Fig. 9 shows to an audience the diminution of resistance of pure copper wire when cooled in liquid hydrogen, in contrast to liquid air. An incandescent lamp c has been placed in circuit with a fine coil of copper wire A, immersed in liquid air, the resistance being so adjusted that the filament in c is just visible when the current passes under these conditions. Now, on removing the coil from the liquid-air vessel and placing it in another similar vessel filled with liquid hydrogen, a great increase in the brilliancy of the lamp is observed. As a matter of fact, the sample of copper has its resistance in liquid air reduced to about one-twentieth of what it is at the temperature of melting ice, whereas in liquid hydrogen the resistance is reduced to one-hundredth of the same amount. In other words, the resistance in liquid hydrogen is only about one-fifth of what it is in liquid air. The interesting point, however, is that theoretically we should infer, from experiments made at higher temperatures, that at a temperature of -223° C. the copper should have no resistance, or it should have become a perfect conductor. As this is not the case, even at the temperature of -253°, we must infer that the curve co-relating resistance and temperature tends to become asymptotic at the lowest temperatures.

Liquid hydrogen is a most useful agent for the production of high vacua and for the separation of gases from air that may be more volatile than oxygen or nitrogen. An experiment illustrating the production of a high vacuum is shown in Fig. 10, where A is the large electric discharging tube to which has been attached a narrow glass tube twice bent at right angles, and terminating in a bulb at the end for immersion in the liquid hydrogen. The rapidity with which the vacuum is attained is shown by the rate at which the striation in the tube changes and the phosphorescent state supervenes. Another rough illustration of the application of cold to effect the separation of a complex mixture of gases is shown in Fig. 8. Coal-gas is passed in succession through the U-tubes F, G, and H made of ordinary gaspipe, having small holes at B, C, D, and E, in order that a flame may be produced before and after each vessel is passed. Each of the U-tubes is placed in a vacuum vessel, and the first cooling substance the gas in its transit meets is solid carbonic acid in F, then liquid air in G, and finally liquid hydrogen in H. At the temperature of the carbonic acid bath, all the easily condensable hydrocarbons separate, and consequently the flame c is less luminous than B. The liquid air bath condenses the ethylene and a large part of the marsh gas, and allows the carbonic oxide and the hydrogen to pass through, so that flame D is less luminous than C. Finally, after the liquid hydrogen bath, nothing escapes condensation but free hydrogen, the carbonic oxide and any marsh gas being solidified; the result is, the flame E is almost invisible.

A really practical application of liquid hydrogen is the purification of helium obtained from the gases emitted by the mineral springs of Bath. Although the helium only amounts to one-thousandth part by volume—the nine hundred and ninety-nine being chiefly nitrogen—yet the low temperature method of separation can be successfully applied.

Now that we know definitely the approximate values of some of the more important physical constants of liquid hydrogen, it is interesting to look back at the values that have been deduced—say for such a constant as the density—by various workers using entirely different methods. The following table gives some of the more important values of the density of hydrogen under the different conditions in which it enters into organic and inorganic bodies.

Density of Hydrogen in Different Conditions.

Kopp	Organic bodies	0.18
Amagat	Limit of gaseous compression	0.12
Wroblewski	Van der Waals' equation	0.027*
Van der Waals..	Superior limit of density	0.82
Graham	Palladium alloy	2.0
Dewar	Palladium alloy	0.63
Dewar	Liquid hydrogen at B.P.	0.07

* Critical density.

My density at the boiling-point agrees substantially with that which can be deduced from Wroblewski's form of the Van der Waals' equation. The deduced densities of Kopp for organic bodies and Amagat for gaseous compression are both about the same value, and may be taken as a mean to be twice the observed density of hydrogen in the liquid state. The conclusions of Graham and myself, touching the density of the hydrogen in the so-called alloy of palladium, must be regarded as altogether exceptional. Even my value would exceed the density of the stuff constituting the real gas molecule, according to the theory of Van Der Waals. In order to harmonise the palladium hydrogen results with those deduced from the study of organic bodies, we must assume that, during the formation of the so-called hydrogenium, a condensation of the palladium sufficient to increase its density by one-fifth must take place. This is by no means an unreasonable hypothesis. The mode of determining the density of hydrogen at its melting-point has been previously described and found to be 0.086. In the same way the approximate values for the densities of nitrogen and oxygen at their melting-points have been found, their respective values being 1.07 and 1.27. The following table shows the comparison between my results and those given by Amagat for high gaseous compressions:—

Densities.

	Liquid Melting-point.	Gas, 3000 atmospheres.	Limiting value, 4000 atmospheres.
Hydrogen ..	0.086	0.097	0.12
Nitrogen ..	1.1	0.833	0.12
Oxygen ..	1.27	1.127	1.25

It will be noted that the density of gaseous hydrogen at 30.0 atmospheres is actually greater than the maximum density of the liquid state; but neither in the case of nitrogen nor oxygen does the density at the same pressure reach the fluid density. Amagat's limiting value for oxygen under 4000 atmospheres would, however, be almost identical with mine.

During the course of my inquiries sufficient data have been accumulated to construct Waterston Formulæ giving the approximate densities of liquid hydrogen, nitrogen, and oxygen in each case through a wide range of temperature. The equation for each substance is given in the following table:—

Liquid Atomic Volumes,

Hydrogen =	23.3 - 8.64 log (32° - t)
Nitrogen =	30.0 - 11.00 log (127° - t)
Oxygen =	32.6 - 10.22 log (155° - t)

	Absolute Zero.	Observed at Melting-point.
1. Atomic volume of hydrogen	10.3	11.7
2. " " "	12.8	13.1
3. " " nitrogen	10.20	12.6
4. " " oxygen		

From these formulæ we find the respective hypothetical atomic volumes of hydrogen, nitrogen, and oxygen at the absolute zero to be 10.3, 12.8, and 10.2. My observed minimum fluid volumes were 11.7, 13, and 12.6. The coefficients of expansion of the liquids, taken in the same order at their respective boiling-points, are 0.024, 0.0036, and 0.0046. Thus liquid hydrogen has a coefficient of expansion five times greater than that of liquid oxygen. Further inquiry will enable the constants in these equa-

tions to be determined with greater accuracy. In the meantime, however, they give us general ideas of the order of magnitude of the quantities involved.

I have to thank Mr. Robert Lennox for efficient aid in the arrangement and execution of the difficult experiments you have witnessed. Mr. Heath has also heartily assisted in the preparations.

ON THE SILICO-VANADIO-MOLYBDATES.

By C. FRIEDHEIM and C. CASTENDYCK.

Preparation of Silico-vanadio-molybdate of Ammonium—800 grms. of yellow silico-molybdate of ammonium $2(\text{NH}_4)_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{MoO}_3 + 8\text{H}_2\text{O}$ are put in suspension in 1.5 litres of water; this is then heated to boiling-point on the water-bath, and, gradually, 180 grms. of white vanadate of ammonium, VO_3NH_4 , are added, and allowed to dissolve completely.

The resulting very deep red solution is evaporated down to 1 litre at the lowest possible temperature, and finally to dryness in a desiccator.

It first of all deposits brilliant red crystals, very soluble in water, then microcrystalline crusts or felted masses of a yellow or brownish-red colour, only slightly soluble in water. The first body is a silico-vanadio-molybdate; as it cannot be re-crystallised in water without alteration it must be separated mechanically from the other products. These other salts are vanadio-molybdates:—

Microcrystalline Crusts—

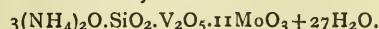
$2(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 5\text{MoO}_3 + 8\text{H}_2\text{O}$..	Yellow.
$(\text{NH}_4)_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{MoO}_3 + 4\text{H}_2\text{O}$..	Yellowish green.
$2(\text{NH}_4)_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 4\text{MoO}_3 + 11\text{H}_2\text{O}$..	Yellowish brown.

Felted Needles—

$(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 2\text{MoO}_3 + 8\text{H}_2\text{O}$..	Reddish brown.
$4(\text{NH}_4)_2\text{O} \cdot 12\text{V}_2\text{O}_5 \cdot 5\text{MoO}_3 + 24\text{H}_2\text{O}$	Brownish red.

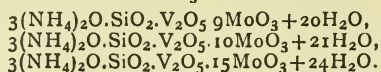
Analysis of the Silico-vanadio-molybdate.—After having heated very carefully to drive off the water and the ammonia, the material is calcined in a combustion tube in a current of hydrochloric acid gas; oxychlorides of vanadium and molybdenum are thus volatilised and collected in an absorption apparatus full of water. But as this volatilisation would never be really completed, the operation is interrupted, and the calcination finished in a current of air, which peroxidises the lower oxides of vanadium and molybdenum which may have been formed. If the calcination in hydrochloric acid gas is then continued, the metals are entirely volatilised, and pure silica is left in the boat. The contents of the absorption tube are treated with sulphuretted hydrogen under pressure, which completely precipitates the molybdenum as MoS_3 , quite free from vanadium, and easy to estimate as MoO_3 . As for the estimation of the vanadium, the simplest method is to make another determination on a fresh sample in the hydrochloric solution, also containing molybdenum, estimating the vanadium by the iodometric method, according to Friedheim and Euler (*Berichte*, vol. xlviii., p. 2061).

Composition and Properties of the Silico-vanadio-molybdate of Ammonium.—By the above method the composition of this body is found to be—



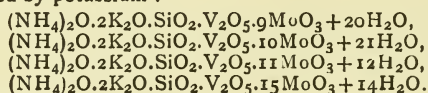
Dilute hydrochloric and sulphuric acids decompose it partially with a deposit of silica or the other microcrystalline salts; ammonia also reacts on it, giving a deposit of silica, and decolorising the solution. The salts of the heavy metals give coloured precipitates, often crystalline; the salts of barium give, after a time, crystals containing ammonia and barium with the three acids. Pure water also decomposes silico-vanadio-molybdate of ammonium. By evaporating the solution other salts were obtained,

only differing in composition from the original salt by the number of molecules of MoO_3 and of water:—



The salts containing 9MoO_3 and 15MoO_3 can be re-crystallised in water without change; the others have a tendency to become transformed into these latter under the action of water. They all give special precipitates with the salts of the heavy metals.

When treated in cold saturated solution with a saturated solution of potassic chloride they give orange-coloured precipitates, in which two-thirds of the ammonia are replaced by potassium:—

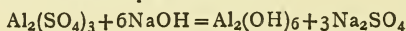


—*Berichte*, vol. xxxii., p. 1611.

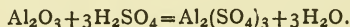
VOLUMETRIC DETERMINATION OF ALUMINA FOR TECHNICAL PURPOSES.

By C. R. GYZANDER.

THE method to be described makes no claim of being original, but does give with ease practically correct results, in a very short time comparatively speaking. It is based on these simple reactions—



and—



Many observers have found that a correct determination of the sulphuric acid in sulphate of alumina is not possible when using normal caustic soda solution, on account of the formation of basic salts, which render the results too low. My own observations corroborate these results and show also that it is useless to employ a factor for correction, as the relation between acid and base, in the salt thrown down by the caustic soda, differed greatly under different conditions. To overcome this difficulty, it has been proposed to convert the sulphate into chloride, by adding an excess of barium chloride solution. Though correct results may be obtained in this way, it offers no particular advantage, because, if the titration is carried on in the presence of the barium sulphate thrown down, the end-point is very obscure, the results much too high and seldom twice alike. Separating the barium sulphate by filtration gives sharp end-point, but it consumes a good deal of time and introduces a source of error from incomplete washing. Without entering into details of experiments which led to the adoption of the following method, I will at once state that, when using a solution of caustic soda not over one-third normal, the results are in accord with the reactions quoted. Though the results are equally good with sulphates, chlorides, and nitrates, the present article treats exclusively of the sulphate, of which three distinct varieties are met with in trade. First, sulphates made from pure, artificial, hydrate of alumina; second, sulphates made from bauxite; and third, sulphates containing zinc sulphate. The first is practically pure sulphate of alumina, containing only a very small amount of silica and sodium sulphate with a mere insignificant trace of iron. The second contains in addition to sulphate of alumina, ferrous and ferric sulphate, mixed or singly. The third contains, in addition to what has already been mentioned, zinc sulphate, and all three are liable to contain copper or arsenic or both, and are either normal, technically termed neutral, basic, or acid. Reagents needed for the analysis are, caustic soda solution free from aluminate and carbonate, and distilled water free from carbon dioxide and ammonia, together

with methyl-orange and phenolphthalein as indicators. By using *caustic soda made from sodium* and manufactured by a reliable firm, an alkali free from alumina may be obtained, and from this one may readily eliminate any carbonates present by treatment with barium hydrate solution, shaking and settling. The clear liquid is then carefully titrated and diluted to the required strength. An aqueous solution of sulphuric acid, of the same strength as the caustic soda solution, is also needed.

As pure potash alum formed the experimental material, its preparation will now be described. I may, however, first remark that the results here reported are based on common atomic weights, and potash alum, in consequence, contains 10.85 per cent $\text{Al}_2(\text{SO}_4)_3$. According to the more recently revised atomic weights, potash alum contains 10.77 per cent $\text{Al}_2(\text{SO}_4)_3$, but, although this lower figure may be more correct, the difference of 0.08 per cent is, for all practical purposes, negligible.

Preparation of Pure Potash Alum.

A hot, saturated, and filtered solution of best procurable potash alum is left to crystallise, the mother-liquor poured off, the crystals washed with some cold water, and a hot saturated solution again made from these crystals in a beaker, which is then placed in a dish of cold water, and the liquid is stirred while cooling. A crop of small crystals is the result. These are drained in a glass funnel, with perforated platinum cone, by means of a suction-pump. When no more water drops off the funnel, the alum is transferred to a sheet of white filter-paper and pressed, until no more wet spots appear on the paper; then transferred to another filter-paper, placed on a warm radiator, and moved about with a horn spatula, until it has the appearance of a perfectly dry, sandy white powder. The alum was transferred to a dry glass stoppered bottle for use.

Determination of Water in the Alum.

1.3099 grms. were weighed in a covered platinum crucible and mixed with recently and strongly ignited pure lime, then covered with some more lime, the crucible cover put on, and the weight ascertained. The crucible was then heated to dull redness over a Bunsen flame and kept so for 15 minutes. It was then cooled in a desiccator and the loss in weight ascertained. The heating was continued for another 15 minutes, after which it was again cooled and weighed. The weight remained constant and the loss of water was 0.5961 grm., or 45.51 per cent, indicating that the alum was pure.

Of this alum, quantities equivalent to 10 grms. of from 50 to 100 per cent $\text{Al}_2(\text{SO}_4)_3$ were weighed and dissolved in a litre of distilled water, and furnished solutions containing known quantities of pure $\text{Al}_2(\text{SO}_4)_3$.

Standard Caustic Solution.

This was made by diluting the previously mentioned, purified and settled, caustic soda solution so that one litre contained 11.65 grms. of NaOH . I will refer to this as *standard soda solution*. 100 c.c. neutralise exactly 3.7862 grms. acid sodium oxalate $\text{NaHC}_2\text{O}_4 + \text{aq.}$ with phenolphthalein as indicator. I prefer this salt to oxalic acid, as it is easily prepared pure and, unlike oxalic acid, is unalterable in air or over sulphuric acid. I prepare it as follows:—To a hot, saturated, and filtered solution of pure oxalic acid was added a hot, saturated, and filtered solution of pure sodium carbonate, so proportioned that there was a slight excess of oxalic acid over what was required for the acid oxalate. The precipitated salt was drained by suction, in a funnel, pressed between filter paper, and dried over sulphuric acid in a desiccator.

Another caustic soda solution, so diluted that 100 c.c. neutralised 1.1370 grms. of acid sodium oxalate, with phenolphthalein as indicator, was also made, and will be referred to as *dilute standard soda solution*.

With the standard soda solution the burette reading corresponds to per cent Al_2O_3 , and with the dilute

standard to per cent $\text{Al}_2(\text{SO}_4)_3$, when half a grm. of sulphate is used for the titration.

Sulphuric acid of such strength that 100 c.c. neutralised an equal volume of standard soda solution was also made and will be referred to as *standard acid*.

One grm. methyl orange dissolved in one litre of water will be referred to as methyl indicator, while one grm. of phenolphthalein in 500 c.c. alcohol will be referred to as phenol indicator.

Analysis of Hydrate Sulphate.

Dissolve 10 grms. of the salt to be tested in boiling water and filter; wash the filter thoroughly, dry and incinerate it, and determine insoluble. Cool the filtrate, and make it up to 1 litre with distilled water; mix thoroughly by shaking; use 50 c.c. for the titration, and add 2 drops of methyl and 4 drops of phenol indicator, 2 c.c. standard acid, and 100 c.c. distilled water; run in standard soda solution slowly, drop by drop and with constant stirring, for some time between each addition of caustic, until the colour changes from pink to orange, not yellow.

If the sulphate was normal, it will require exactly 2 c.c. standard soda solution; if it was basic, then the excess of alumina will form sulphate with the sulphuric acid added, and, in consequence, less than 2 c.c. of standard caustic will be required to neutralise the solution. In that case, the difference between the sulphuric acid and standard soda used gives per cent of basic alumina. Continue to run in standard soda solution (starting from 0 of the burette) in a moderate stream and with constant stirring, until a faint but permanent pink is obtained. The number of cubic centimetres of standard soda solution used indicates per cent total Al_2O_3 . From it, subtract the basic and multiply the remainder by 3.33, and the result is per cent $\text{Al}_2(\text{SO}_4)_3$.

The correct end-point for neutrality with methyl-orange, for sulphates up to 60 per cent $\text{Al}_2(\text{SO}_4)_3$, is obtained by comparison with the tint of a solution of 50 c.c. pure potash alum (10 grms. per litre), to which is added 2 drops of methyl indicator and 100 c.c. distilled water. The following solutions were made:—

	Grms. per litre.		Per cent $\text{Al}_2(\text{SO}_4)_3$.	or	Per cent Al_2O_3 .
1.	10	=	36.13	or	10.85
2.	13.8389	=	50.00	"	15.01
3.	15.2228	=	55.00	"	16.51
4.	16.0531	=	58.00	"	17.41
5.	16.6066	=	60.00	"	18.01
6.	19.3744	=	70.00	"	21.02
7.	22.1422	=	80.00	"	24.02
8.	24.9100	=	90.00	"	27.02
9.	27.6778	=	100.00	"	30.03

Each of these solutions were tested with *standard* and *dilute standard* soda solution.

To 50 c.c. of each solution were added 2 drops methyl, 4 drops phenol indicator, and 100 c.c. distilled water. The caustic solution was run in, in a rapid succession of drops and with constant stirring, until pink began to appear; then slowly, drop by drop, until a faint—but distinct and permanent—pink was obtained, and which did not fade after continued stirring.

The phenol end-point is sharpest at about 30° C. Above this temperature, the results are incorrect and in excess of the theoretical amount, as alumina at high temperatures is acid towards phenolphthalein. Below 20° C. the reaction is very tardy, and the end-point, in consequence, obscure.

Towards the end of the reaction, the precipitated alumina forms with phenolphthalein a pink-coloured lake, which persists even after the most vigorous stirring; methyl-orange masks this pink colour, and thus helps to sharpen the phenol end-point. This residuary colour becomes more troublesome at low temperatures and with strong sulphates, and for that reason I add 3 drops of

methyl indicator to sulphates with over 60 per cent $\text{Al}_2(\text{SO}_4)_3$. The results recorded below are the average of five determinations.

	Standard.			Dilute standard.	
	Found. Al_2O_3 .	Calculated. $\text{Al}_2(\text{SO}_4)_3$.	Error.	Found. $\text{Al}_2(\text{SO}_4)_3$.	Error.
1.	10.84	36.10	-0.03	36.05	-0.08
2.	14.96	49.82	-0.18	49.90	-0.10
3.	16.48	54.88	-0.12	54.84	-0.16
4.	17.34	57.74	-0.26	57.88	-0.12
5.	17.94	59.74	-0.26	59.88	-0.12
6.	20.88	69.53	-0.47	69.92	-0.08
7.	23.88	79.52	-0.48	79.92	-0.08
8.	26.84	89.38	-0.62	90.05	+0.02
9.	29.82	99.30	-0.70	99.94	-0.06

From these figures, it will be seen that the dilute standard gives better results, but that, for practical purposes, the *standard* is correct for sulphates up to 60 per cent $\text{Al}_2(\text{SO}_4)_3$.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1901.

Mr. C. E. GROVES, F.R.S., Vice-President, in the Chair.

MESSRS. George Harker and T. G. Donnan were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harry Burrows, The Green, Southgate, N.; Kenneth Macomb Chance, Lawnside, Edgbaston; William Clifford, 1, Avondale Road, Wolverhampton; John Kemp Smith Dixon, Gothic House, Birstall, nr. Leeds; Alfred Vincent Elsdon, Storrington, Pulborough, Sussex; Lewis Eynon, 57, Darent Road, Stamford Hill, N.; Frederick Ferrand, 13, Torrington Street, Hopwood, Heywood; John Oliver Ferrier, Colombo, Ceylon; George Frederick Holdcroft, 253, Oxford Street, Manchester; Frank Sturdy Sinnatt, Glenside, Church Lane, Moston, Manchester; Lyon Viccars Turner, Crescent Lodge, St. John's, S.E.

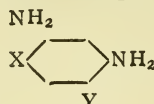
A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. Frederick T. Allen, B.Sc.; Arthur Baker; Thomas Thorne Baker; Walter Craven Ball, B.A.; Andrew Russell Bennett; Harding Bickford; Henry Boyers; William Burton, B.Sc.; William Cormack; Samuel Irwin Crookes; Frank Crossley; John Howard Davidson, B.Sc.; Francis Davis; Robert English; Henry Whippell Gadd; T. K. Gajjar, M.A., B.Sc.; Hermann Charles T. Gardner; Edward Gillman; William Peer Groves, B.A.; Herbert Blackmore Hammond; Herbert Harding; Edwin Hobson; Beresford Ingram, B.A.; J. S. Jameson; Charles H. Johnson, M.B., Ch.M.; Walter Henry Jollymann; James David Kettle, B.Sc.; J. Bruce-Kingsmill, M.A., B.Sc.; Alfred Tabois Larter; Albert W. D. Leahy; Peter MacDonald; Charles K. Millard, M.D., D.Sc.; Edward Holl Miller; Christian Müller; Herbert Simpson Newbould; Albert Edward Parkes; Walter Herbert Pay; Charles James Tomlin Pollitt; Rowland Samuel Potter; Charles Leonard Royle; John Henry Ryffel, B.A., B.Sc.; Allan Sandford; George Charlton Scott; Edward Charles Sherwood, M.A.; Norman Smith, B.Sc.; Robert Stephenson, jun., B.A.; William Henry Templeman; Harold Foy F. Varley; Frank Wade; Merton Wager; Herbert George Wallace; Philip Lewington Whitehouse.

Of the following papers, those marked * were read:—

*161. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds." By G. T. MORGAN, D.Sc.

The disubstituted derivatives of *m*-phenylenediamine having one free para-ortho-position with reference to the

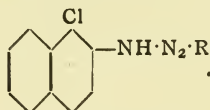
amino-radicles interact readily with diazonium salts, giving rise to aminoazo-compounds in almost theoretical quantities. The diamines of the general formula—



having substituents in both the para-ortho-positions do not easily condense with diazonium salts, and the yield of aminoazo-compound is very poor.

The bases of both series, however, combine with primulin diazotised on the cotton fibre, the diamines of the first series giving rise to reddish-brown azo-compounds, whilst those of the second series furnish colouring matters having a brownish-yellow tint.

Although the interaction of β -naphthylamine and a diazonium salt leads to the direct formation of an *o*-aminoazo-derivative containing the diazo-residue $\text{R}\cdot\text{N}_2$ —in the α -position contiguous to the amino-group, yet 1-chloro-2-naphthylamine, under similar conditions, yields stable diazoamines of the type—



In this compound, the azo-group has no tendency to shift into the aromatic nucleus, this transference being apparently prevented by the presence of the chlorine atom in the adjacent ortho-position.

The following acyl derivatives were prepared in characterising certain of the diamines employed in this investigation. *Diformyl-4:6-diamino-1:3-xylene*, needles, m. p. 182–183°, the corresponding *diacetyl* and *dibenzoyl* derivatives, m. p. respectively at above 260° and 253°; *diformyl-2:4-diamino-1:3-xylene*, m. p. 219–220°, the *diacetyl* derivative, m. p. above 260°, and the *dibenzoyl* derivative, m. p. 232°; *diformyl-5-chloro-2:4-tolylenediamine*, silky needles, m. p. 166°, the *benzoyl* derivative, m. p. 205°.

The following azo-compounds were produced in illustrating the behaviour of the two series of diamines towards diazonium salts. *Benzene-5-azo-2:4-diamino-1:3-xylene*, readily produced from 2:4-diamino-1:3-xylene, brown needles, m. p. 208–209°; its *diacetyl* derivative, m. p. above 260°; *diacetylbenzene-5-azo-2:4-tolylenediamine*, m. p. 216–217°.

Benzene-5-azo-4:6-diamino-1:3-xylene, obtained with some difficulty and in small yield from 4:6-diamino-1:3-xylene, forms deep red plates, m. p. 182–183°; its *diacetyl* derivative, m. p. above 260°. *p-Toluene-5-azo-4:6-diamino-1:3-xylene* resembles its lower homologue, and melts at 165–166°. Small yields of *benzene-3-azo-5-chloro-2:4-tolylenediamine* and its *p-toluene* homologue are produced from 5-chloro-2:4-tolylenediamine; they crystallise in dark, brownish-red plates, m. p. 147° and 152° respectively; the *dibenzoyl* derivative of the former azo-compound melts at 236–237°.

Benzene-6-azo-2-chloro-3:5-tolylenediamine, obtained in theoretical quantity from 2-chloro-3:5-tolylenediamine, forms orange-red, acicular prisms, m. p. 134°; its *diacetyl* and *dibenzoyl* derivatives crystallise in orange coloured needles, m. p. 251° and 233° respectively.

1-Chloro-2-naphthylamine yields the following diazoamines when treated with the appropriate diazonium chloride. *2-Diazoamino-1-chloronaphthalene*, $\text{ClC}_{10}\text{H}_6\cdot\text{N}_3\text{H}\cdot\text{C}_{10}\text{H}_6\text{Cl}$, produced by the action of 1-chloro-2-naphthalenediazonium chloride, crystallises in golden-yellow needles, m. p. 152°.

p-Nitrobenzene-2-diazoamino-1-chloronaphthalene, $\text{NO}_2\text{C}_6\text{H}_4\cdot\text{N}_3\text{H}\cdot\text{C}_{10}\text{H}_6\text{Cl}$, obtained from *p*-nitrobenzediazonium chloride and 1-chloro-2-naphthylamine, or from 1-chloro-2-naphthalenediazonium chloride and *p*-nitraniline, crystallises in brownish-yellow leaflets; it melts and decomposes at 197–198°.

Its production by the two processes indicated shows that Kekulé's rule for the formation of mixed benzenoid diazoamines applies also to those containing naphthalene residues. The *ethyl* derivative, produced by the direct ethylation of the preceding compound, separates from benzene in hard, yellow, prismatic crystals, m. p. 193–194°.

DISCUSSION.

Mr. EVERSLED asked whether the primulin compounds described were only obtainable on the fibre, and if so, whether similar compounds could be obtained outside the fibre by using dehydrothioparatoluidine instead of primulin.

Dr. HEWITT inquired whether the author expected to obtain three distinct ethyl derivatives of unsymmetrical diazoamino compounds, or whether the derivative obtained by alkylation would not be a mixture of the other two ethyl derivatives obtained by coupling diazotised amines with monoethylamines. Such cases had already been observed by Meldola. The earlier idea that in the benzene series *p*-azo-compounds exclusively result when the para-position is free can no longer be held to be absolutely true. Bamberger (*Ber.*, 1900, xxxiii., 3188) has obtained small quantities of ortho-oxyazobenzene mixed with a large amount of the para-isomeride by the action of a phenyldiazonium salt solution on an alkaline solution of phenol.

Dr. MORGAN, in reply, said that the colouring matters produced from diazotised primulin were obtained only on the cotton fibre, this reaction being employed merely as a ready means of ascertaining whether the symmetrically disubstituted diamines react with diazo-compounds. The substances prepared by the action of the simpler diazonium salts (benzediazonium chloride and its *p*-tolyl homologue) on these bases have the appearance of true azo-compounds; they are readily acetylated and benzoyleated without decomposition, and withstand prolonged digestion with boiling hydrochloric acid, either in aqueous or alcoholic solutions, just like the isomeric azo-derivatives obtained from the diamines, in which the diazo-residue enters the ring in a para ortho-position with respect to the amino-radicles.

*162. "The Determination of Available Plant Food in Soils by the Use of Dilute Solvents." By A. D. HALL and F. J. PLYMEN.

The use of various weak acid solvents has been suggested in the analysis of soils, as dissolving out the mineral plant food which may be regarded as immediately "available" for the crop.

In order to ascertain which acid would give the most "critical" results as judged by the known history of the soil, the authors have determined the phosphoric acid that could be extracted from nineteen different soils by a 1 per cent solution of citric acid, by equivalent solutions of hydrochloric and acetic acids, by a saturated solution of carbonic acid, and by an ammoniacal solution of ammonium citrate respectively. Seven of the soils were from plots on the Broadbalk field, Rothamsted, which had been continuously manured in the same manner for forty-two years previously; the remaining twelve were soils of very various origin, which had been the subject of crop experiments, and of which the reaction to phosphatic manuring was well marked. In the same seven soils from the Broadbalk field the authors determined the potash extracted by the same solvents, with the exception of ammonium citrate; five other soils of different origin, whose response or otherwise to potash manuring had been tested by experiment, were also examined. Determinations were made of the phosphoric acid and potash dissolved after long digestion with strong hydrochloric acid, of the loss on ignition, and of the earthy carbonates present in each soil.

The acids did not attack the phosphates and potash in the same way; in the case of phosphoric acid most was dissolved by citric acid, in the case of potash by hydrochloric acid; water charged with carbonic acid generally

dissolved less than the other solvents. In all cases the weak acids gave better indications of the need of the soil for special mineral manuring than was afforded by the determination of the total phosphoric acid or potash present.

Though, as a rule, all the acids gave similar indications as to the relative fertility of the soils, as regards the mineral matters under consideration, certain differences exist in their modes of attack; for example, from the soil of the Broadbalk field, which had received an annual dressing of dung for forty-two years, the weak hydrochloric acid extracted a comparatively smaller proportion of phosphoric acid than the other solvents; hydrochloric acid again had relatively slight action on the phosphates of the nitrated plots. The strength of the acids used affected the amount of phosphoric acid dissolved, and the addition of calcium carbonate to the soil diminished the amount dissolved by citric, but not by acetic or carbonic acids.

Though the differences in the rate of attack which the various acids exhibit in dealing with soils of a different type are related to the varying states of combination of phosphoric acid or potash in the soils, there is still sufficient likeness in the indications afforded by all the acids to negative the idea that any one acid can be found which will discriminate sharply between the "available" and "non-available" mineral plant food.

The authors conclude:—

1. That no sharp distinction can be drawn between "available" and "non-available" phosphoric acid and potash in the soil, and that any process for determining the "available" constituents is an empirical one, dependent on the strength and nature of the acid used.

2. That the weak solvents give information as to the requirements of a given soil for mineral manures of a far more trustworthy nature than that which is afforded by such a solvent as strong hydrochloric acid.

3. That of the acids examined, the 1 per cent solution of citric acid gives results most in agreement with the recorded history of the soil, though there is evidence that the same interpretation cannot be put on results obtained from all types of soil.

DISCUSSION.

Dr. ARMSTRONG said the only way in which the method advocated could be tested was to compare the laboratory results with those afforded by field experiments such as had been made at Rothamsted; and it was remarkable how general was the agreement in that case. But he felt less happy after listening to the account given of this work with other soils; the results did not appear to be so uniformly in favour of Dr. Dyer's method. The conditions offered by soils were obviously very complicated, and it was difficult to believe that so simple a test could afford really comparable results in all cases, especially when applied to soils varying greatly in character. But the case was one in which the decision must be based on considerable experience. Dr. Armstrong took exception to the authors' use of curves in expressing their results, and suggested that only vertical ordinates should be plotted.

Mr. T. S. DYMOND said that this paper was particularly interesting, as one of the soils was a London clay from the "dereli&" grass land of Essex, from a field which manurial trials had shown to be almost devoid of available phosphoric acid. When superphosphate of lime was used, a dressing of nitrate of soda had doubled the produce of hay, while in its absence nitrate of soda failed to give any increase at all. The citric acid-soluble phosphoric acid in the top nine inches of soil amounted, as shown by the authors, to 200 lbs. per acre, while the crop was able to remove no more than 2 lbs., leaving, apparently, no further available phosphoric acid in the soil. Although that quantity might be potentially "available" in the soil, it was not actually available in such land as this, until, by improving its mechanical condition, air was admitted, fermentation encouraged, and carbonic acid produced. The experiment also indicated that the acidity of the root

sap of the grasses and clovers had little, if any, effect in dissolving "available" phosphate. Both on this ground and on the ground that the carbonic acid-soluble phosphoric acid, as shown by the authors, was much lower than the citric acid-soluble phosphoric acid, the use of carbonic acid as a solvent would appear to give a truer idea of the amount of phosphoric acid actually available. No conclusion as to the manurial requirements of such land should be drawn without also taking into account the various circumstances favourable to carbonic acid production.

Mr. F. J. LLOYD said that, as in the case of Dr. Dyer's paper (*Proc.*, 1894, x., 36), no steps seemed to have been taken to allow for the alkaline reaction of the soil. In the 200 grms. used by the authors there might easily be present 4 grms. of calcium carbonate, a quantity which would materially affect the 20 grms. of citric acid in 2 litres of solution, so that the soil was not really subjected to the action of a 1 per cent solvent.

Mr. HALL said, in reply, that the effect produced by calcium carbonate in the soil had not been overlooked. The authors had used a soil to which successive additions of 2, 5, and 10 per cent of calcium carbonate were made before treating with the dilute acid. The amount of phosphoric acid dissolved by the citric acid was diminished with each addition of calcium carbonate, but the attack of acetic and carbonic acids was practically unchanged. The diminution was not, however, proportional to the neutralisation of the acid, because neutral saline solutions themselves had a solvent effect, dissociation doubtless coming into play.

There were discrepancies still to be cleared up in the results furnished by citric acid; probably as was indicated in the paper, for different types of soil different "limits" would have to be taken as indicative of the need of mineral manures.

*163. "On a Method for Determining Small Quantities of Carbonates." By A. D. HALL and E. J. RUSSELL.

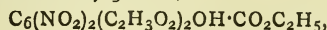
The authors have devised an apparatus for determining small quantities of carbonates in material like soil by measuring the carbon dioxide evolved. The material is placed in a small bulb, the volume of which need not be known, in which the pressure is reduced to an approximate vacuum; the carbonate is decomposed by the admission of dilute sulphuric acid, and the change in pressure thus produced is noted. Connection is then made with a second vacuous bulb of known volume, and the change in pressure again read. From the two changes in pressure the volume of carbon dioxide can be calculated. A knowledge of the volume of the material is not required, and the volume of the carbon dioxide which dissolves in the reacting liquid does not enter into the calculation, since the liquid practically forms part of the unknown volume of the first bulb.

Examples are given of the measurements of carbon dioxide evolved from pure carbonates in known quantity ranging from 0.13 c.c. to 11.26 c.c.

164. "Derivatives of Gallic Acid." By F. B. POWER and F. SHEDDEN.

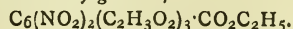
The authors have prepared and described the following derivatives of gallic acid:—

Ethyl dinitrodiacetylgallate,—



was prepared by the nitration of ethyl triacetylgallate, m. p. 133°. It forms lemon-yellow needles, m. p. 165°.

Ethyl dinitrotriacetylgallate,—

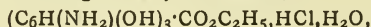


was prepared from the preceding compound by the action of acetic anhydride. It forms colourless needles, m. p. 145–146°, which gradually become yellow. Its cold alcoholic solution gives no reaction with ferric chloride, but, on boiling, a bluish green colour is produced.

Ethyl dinitrogallate, $\text{C}_6(\text{NO}_2)_2(\text{OH})_3\cdot\text{CO}_2\text{C}_2\text{H}_5$.—When an alcoholic solution of ethyl dinitrodiacetylgallate is

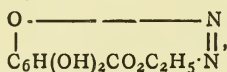
boiled with sodium ethoxide, and allowed to stand, the sodium salt of ethyl dinitrogallate was deposited as a bright red, crystalline powder. From the aqueous solution of the latter, hydrochloric acid precipitates ethyl dinitrogallate in the form of small yellow scales, which melt at 153–154°. The same compound was obtained by boiling ethyl dinitrodiacetyl-gallate with 50 per cent sulphuric acid.

Ethylmonamidogallate hydrochloride,—



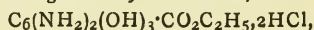
was obtained, together with the diamido-derivative, by the reduction of ethyl dinitrogallate with tin and hydrochloric acid. It forms white, needle-shaped crystals, which melt at 210° with decomposition. It can be precipitated from its aqueous solution by the addition of strong hydrochloric acid.

Diazoethylgallate,—



was obtained by the action of nitrous acid on ethyl monamidogallate. When re-crystallised from dilute acetic acid it forms fine, reddish-brown needles, which melt with sudden decomposition at 182°. When heated with water in a sealed tube at 220° for four hours, the nitrogen is completely eliminated, and ethyl gallate is produced.

Ethyl diamidogallate hydrochloride,—



was obtained, together with the above described mon-amido-derivative, by the reduction of ethyl dinitrogallate. It melts with decomposition at 197°, and is very easily oxidised. It dissolves readily in water, and the solution almost immediately becomes blue, the colour being intensified by the addition of a very little ferric chloride, but destroyed by an excess.

165. "Note on Phosphorus Suboxide." By K. C. BROWNING, M.A.

The author has investigated the following methods used to prepare so-called phosphorus "suboxide."

1. Oxidation of phosphorus, both in the solid state and in solution, by air diluted with carbon dioxide.

2. Action of metals on phosphorus oxychloride.

3. Action of acetic anhydride on sodium hypophosphite.

The results obtained confirm, on the whole, those of Chapman and Lidbury, and of Burgess and Chapman, although the author believes that the suboxide can exist under certain conditions.

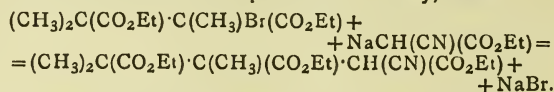
166. "The Bromination of Trimethylsuccinic Acid and the Interaction of Ethyl Bromotrimethylsuccinate and Ethyl Sodiocyanacetate." By W. A. BONE and C. H. G. SPRANKLING.

When trimethylsuccinic acid is heated under pressure to 130° with the calculated quantity of bromine, it is converted into the characteristic white bromotrimethylsuccinic anhydride, m. p. 197–198°. On the other hand, if the bromination be carried out according to the Hell-Volhard-Zelinsky (phosphorus and bromine) method, and the product be poured into alcohol, a mixture of the bromoanhydride and ethyl bromotrimethylsuccinate results, from which it is difficult to obtain the latter substance in a tolerably pure state.

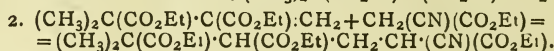
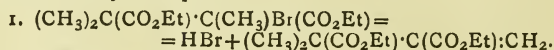
On heating the bromoanhydride with diethylaniline, hydrogen bromide is eliminated, and on afterwards pouring the liquid into a solution of potassium hydroxide, the potassium salt of methylenedimethylsuccinic acid, $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H}) \cdot \text{C}(\text{CO}_2\text{H})\text{CH}_2$, is obtained. The acid melts at 140–141°, its diethyl salt boils at 173–176° (755–760 m.m.), and readily absorbs bromine and hydrogen bromide in the cold.

Ethyl bromotrimethylsuccinate reacts with ethyl sodiocyanacetate with the formation of the cyano-ester, which on hydrolysis yields a tribasic acid, $\text{C}_9\text{H}_{14}\text{O}_6$, melting at 137–138°. This acid is not *i*-camphoronic ($\alpha\beta$ -trimethyl-

tricarballic) acid (m. p. 169–173°), which would have resulted had the reaction proceeded normally, thus:—



Most probably the acid is the isomeric $\alpha\alpha$ -dimethylbutane $\alpha\alpha$ - β -tricarboxylic acid, a view which the authors' experiments so far justify, and its formation is explained on the supposition that ethyl bromotrimethylsuccinate, in contact with ethyl sodiocyanacetate, loses hydrogen bromide, forming ethyl methylenedimethylsuccinate, which immediately condenses with ethyl cyanacetate as indicated by the equation:—



The further investigation of the new acid is now being prosecuted.

167. " β -Bromocamphor." By H. E. ARMSTRONG and T. M. LOWRY.

The formation of derivatives of β -bromocamphor on decomposing by heat the sulphobromides of the Reychler series of substituted camphorsulphonic acids has been described in a previous notice (*Proc.*, 1901, p. 217). On treating the unsubstituted sulphobromide in a similar manner, in the spring of the present year, a bromocamphor was obtained, which melted at 76°, very similar to ordinary bromocamphor; but as the melting-point of a mixture of the two substances was 65°, it was clear that they were not identical. By further purification of the substance, the melting-point was raised to 79°. The optical rotatory power of the new compound is very different from that of α -bromocamphor, a solution in acetone containing 3.3 per cent giving $[\alpha]_D = 18^\circ$, the corresponding value for the α -bromocamphor being 143° .

Recently, larger quantities of material have been prepared, and proof has been obtained that the new bromocamphor is the parent term of the β -series by its direct oxidation into β -bromocamphoric acid.

Simultaneously with the authors, Dr. M. O. Forster has obtained β -bromocamphor by simply brominating the isomeride of camphor which he has described under the name of hydroxycamphene. A direct comparison of the products from the two sources has been made, which leaves no doubt as to their identity. Dr. Forster's observations are described independently.

168. " β -Bromocamphor." By M. O. FORSTER.

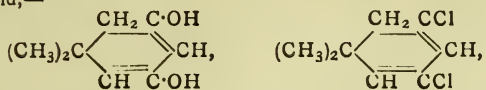
When 1-hydroxycamphene (*Trans.*, 1901, lxxix., 644), dissolved in glacial acetic acid containing sodium acetate (1½ mols.), is treated with a solution of bromine (1 mol) in the same solvent water precipitates a new bromocamphor, which, from the fact that bromine converts it readily into β -dibromocamphor melting at 114°, must be regarded as the monobromocamphor which has the substituent in the unknown β -position. The bearing which this observation has upon the constitution of 1-hydroxycamphene will be discussed in a future communication.

β -Bromocamphor, $\text{C}_{10}\text{H}_{15}\text{OBr}$, crystallises from alcohol in long, colourless, prismatic needles, and separates from petroleum in transparent, well-formed prisms; it melts at 78°, has $[\alpha]_D = +19^\circ$ in alcohol, and $[\alpha]_D = +16^\circ$ in chloroform. Alcoholic potash eliminates bromine from the substance, and converts it into an unsaturated acid which belongs probably to the campholenic series. The oxime crystallises from alcohol in lustrous, rhomboidal plates, which melt at 156°.

169. "Substituted Dihydrobenzenes." Part I. By A. W. CROSSLEY and H. R. LE SUEUR.

When 2:6-diketo-4:4-dimethylhexamethylene (dimethyldihydroresorcinol) is treated with phosphorus pentachloride, both oxygen atoms are removed apparently

as hydroxyl groups, giving rise to 2:6-dichloro 4:4-dimethyldihydrobenzene, a colourless, highly refractive liquid,—



boiling at 91° at 23 m.m. It has a faint odour of turpentine, resinifies slowly on exposure to air, and on boiling with dilute sulphuric acid is re-converted into dimethyldihydroresorcinol. When treated with sodium in moist ethereal solution, both chlorine atoms are replaced by hydrogen atoms, and there results 4:4-dimethyldihydrobenzene, a clear, colourless, mobile liquid, with a marked odour of turpentine, boiling at 111°. It is homologous with the terpenes, which it resembles in chemical behaviour. Thus it decolorises a solution of bromine in chloroform; concentrated sulphuric acid produces a blood-red colour, changing to violet on standing, and with hydrogen bromide it gives a crystalline hydrobromide.

Its properties are being thoroughly investigated, and other similar hydrocarbons are being prepared.

170. "The Part Played by Residual Affinity in the Formation of Substitution Derivatives. The Orienting Influence of Sulphur." By H. E. ARMSTRONG and E. HORTON.

In previous notices, it has been argued that the formation of ortho- and para-substitution derivatives from phenolic and aminic compounds is due to the attractive influence exercised by the oxygen and nitrogen respectively, and experimental evidence has been adduced which shows that if the phenolic or aminic hydrogen be displaced by hydrocarbon or acid radicles, the "activity" of the oxygen or nitrogen is more or less diminished, if not entirely destroyed; in other words, that the "residual affinity" of the negative element becomes weakened in some cases to the point of being inoperative (compare *Proc.*, 1899, xv., 176; 1900, xvi., 157; *B. A. Report*, 1899, 683).

Although applied to the explanation of the formation of substitution derivatives generally as far back as 1887 (*Trans.*, li., 268), the doctrine of "residual affinity" has not hitherto received the attention it perhaps deserves in this connection; we seem to have forgotten that the conception that addition precedes substitution dates back at least to Kekulé's famous paper on the valency of carbon (1858). But now that the doctrine of residual affinity has been re-discovered in Germany by Thiele, and advocated by von Baeyer (*Ber.*, 1901, xxxiv., 2686), it appears likely to become the fashion, and there is some chance that at last justice may be done to the peculiar qualities of the negative elements; the tendency at the moment to credit oxygen with full tetrad functions is proof, however, that unless care be taken the doctrine will be pushed to unwarrantable extremes.

In studying the influence of residual affinity, sulphur is an element of peculiar interest deserving of far more attention than it has hitherto received; its lethargic behaviour in benzenoid compounds is especially remarkable. To obtain further knowledge of these compounds, the authors are engaged in contrasting the thiobenzenoid ethers with the corresponding oxygen ethers.

Methyl and ethyl phenylsulphides are readily sulphated, yielding para-acids, which afford well-defined salts, &c. On oxidation by permanganate, the thiosulphonates are converted into corresponding sulphonesulphonates. If an aqueous solution of the thiosulphonate be subjected to the action of bromine, it is converted wholly into the corresponding sulphoxide-sulphonate; for example, $\text{EtS} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{K} + \text{Br}_2 + \text{OH}_2 = \text{EtSO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{K} + 2\text{HBr}$, the bromine acting only as an oxidising agent. As it was probable that oxidation was due to the formation of hypobromous acid, in the expectation that if this were prevented from forming, bromine would be without action, the salt was brominated in presence of muriatic acid; under these conditions, the salt was converted

entirely into the ortho-bromo-thiosulphonate. It seems, therefore, that, if prevented from undergoing oxidation, sulphur may behave as oxygen does; but the thioether-sulphonates are far more stable than the oxygen-ether-sulphonates, as the sulphy-group is not displaced from them by bromine.

Mr. Lewis has ascertained that muriatic acid has, in some cases, a distinct influence on the course of change on brominating the oxygen-ether-sulphonates, and that it promotes the formation of the ortho-bromosulphonate whilst diminishing the extent to which the sulphonic group is displaced.

Library Catalogue.

A new Catalogue of the Library, arranged under authors' names and subjects in accordance with the system adopted in indexing the Society's publications, is ready for the press. Fellows who desire a copy of the catalogue, at a cost of 2s. 6d., are requested to send in their names to the Secretaries not later than January 31st, 1902.

If a sufficient number of names is not received, the catalogue will not be printed.

Memorial Lectures, 1893—1900.

Fellows can now obtain copies of the volume of collected Memorial Lectures on application to the Assistant Secretary, price 7s. 6d. post free.

PHYSICAL SOCIETY.

Ordinary Meeting, December 13th, 1901.

Prof. S. P. THOMPSON, President, in the Chair.

THE following papers were read by the SECRETARY:—

"On Circular Filaments or Circular Magnetic Shells equivalent to Circular Coils, and on the equivalent Radius of a Coil." By Prof. T. R. LYLE.

It is shown that we can represent the magnetic action of any coil by replacing it by one or more filamentary circuits in which currents circulate bearing a simple relation to the actual current in the coil. If the axial and radial dimensions of the coil in question are the same, then the external magnetic action can be represented by that of one filamentary circuit. If the axial breadth is greater than the radial depth we must employ two filaments of equal radii separated by an axial distance; and if the opposite condition holds, two circular filaments of different radii lying in the same plane perpendicular to the axis of figure of the coil. In the case of coils in which the axial and radial dimensions are equal, a modification of Bosscha's method is described which yields the equivalent radii directly as the result of length measurements. If the axial and radial dimensions are not equal, it is shown that the method is still applicable provided that the ratio of the resistances of the Bosscha comparison be altered in a ratio depending on these dimensions. Apparatus for carrying out the experiment is described, and applications to some classical cases are given. It is also pointed out that the correction for finite length of magnet in Bosscha's (or the present) method of comparison is in general far from negligible. The formulæ used are based on the expansion of the potential of a coil for points on its axis and terms up to the fourth have been included, but the effect of neglecting higher terms is not investigated.

The SECRETARY read a letter from Lord Rayleigh in which he stated that the length of the magnet used in determining the constant of the current balance used in the determination of the electrochemical equivalent of silver was one-tenth of an inch, and the error due to neglecting this was less than one part in ten thousand.

Mr. W. WATSON expressed his interest in the method because it reduced the ordinary arithmetical calculations,

and drew attention to some advantages of the practical applications.

The CHAIRMAN said it was a useful step to reduce the action of a rectangular coil to that of two filaments. In the case of a tangent galvanometer with one coil, if the channel is cut to take nine turns axially and eleven radially, then the equivalent radius is equal to the mean radius.

"On Air-pressures used in Playing Brass Instruments." By DR. E. H. BARTON and MR. S. C. LAWS.

It is well known that in playing upon the "brass" or "woodwind" instruments of the orchestra, the particular note, at any instant desired, is produced by the simultaneous use of the mechanism of the instrument and the corresponding "embouchure" through which air at a suitable pressure is driven by the performer. The object of the paper is to find how the air pressure required to sound the different notes varies with (1) the pitch of the note (2) its loudness, (3) the fingering or other manipulation of the instrument, (4) on the instrument itself. Experiments were made with the tenor trombone, the trumpet, and the cornet, and the pressures were taken by a water-manometer connected to the performer's mouth by an india-rubber tube terminating in a glass nozzle which could be held by the side teeth. The following inferences are drawn from the experiments:—(1) Other things being equal, the louder the note the greater the pressure. (2) The higher the pitch of the note played on a given instrument the greater the air-pressure used. (3) The curves formed by plotting the logarithms of the frequencies of the notes as abscissæ and the pressures as ordinates are straight lines. (4) The air-pressure required to sound any note with given intensity is approximately proportional to its pitch defined logarithmically. (5) Where alternative positions or fingerings are used for the same note the pressures are practically the same. (6) The pressures for identical notes on trumpet and cornet are almost the same for any given intensity, but very much less than those for the same notes on the trombone. (7) The pressures used for loud low notes may exceed those for soft high notes.

Prof. J. D. EVERETT said the paper was an interesting attempt to make a quantitative connection between theory and practice, and the linear law connecting logarithmic frequencies and pressures came out well from the experiments. He asked if the pressure necessarily depended on the skill of the operator.

Mr. D. J. BLAKLEY said that soon after the publication of Dr. Stone's experiments on this subject he followed up the matter by experiments of his own, using a simple water-pressure gauge. The general results agreed fairly well with those given in the paper, but from them one law appeared to be deducible which was not suggested by Dr. Barton and Mr. Laws, and which greatly modified their conclusion (4). His observations showed that when the intensity was reduced to the lowest possible point for each of the notes in a given series, the resulting minimum pressures were directly proportional to the frequencies and not to the frequencies as defined logarithmically. It was further noticed that whether a given note—as, say, B₂ of 240 vibrations—was sounded as the eighth harmonic of a contrabass, the fourth harmonic of a tenor trombone or euphonium, or as the second harmonic of a cornet, the result was approximately the same. The minimum pressure at which any note can be sounded appeared to depend solely upon its absolute pitch and not upon the place of the note, upon the instrument used, or upon the calibre or total mass of air in the instrument.

Mr. WATSON suggested that if different gases were used to blow the instruments the results might depend upon the velocity of sound in the gas used.

"On a New Hygrometric Method." By MR. E. B. H. WADE.

In this method a thermometer is wetted, not with water but with sulphuric acid of such a strength that the temperature of the acid bulb is close to that of the dry bulb. The maximum tension of the acid at any temperature is

known from Regnault's work, and two or more determinations with this instrument and with a wet and dry bulb hygrometer at the same time enable the constants of both instruments to be determined. If the difference between the acid bulb and the dry bulb is less than 2° the constant remains fixed over a large range. Experiments show that the readings of the instrument are not affected by ventilation, and since the difference between the temperatures of the bulbs is small errors in the determination of the constant are unimportant.

Prof. J. D. EVERETT criticised the paper at length and said he could not commend the method described.

Prof. A. S. HERSCHEL said that tables might be constructed for use with the author's instrument similar to those used by Glaisher with the ordinary wet and dry bulb hygrometer.

Mr. W. WATSON replied to some of Prof. Everett's remarks, and pointed out some of the advantages of the method described in the paper.

The Society then adjourned until January 24th, 1902.

NOTICES OF BOOKS.

The Elementary Principles of Chemistry. By A. V. E. YOUNG. New York: D. Appleton & Co., 1901. Pp. 358.

THE arrangement of this volume is as remarkable as it is confusing. It is apparently divided into two parts; the first part called "The Elementary Principles of Chemistry," extends to 252 pages, including an index of eight pages. The book is properly paged, but this paging is entirely useless, as no reference to any page number is made either in the index or the table of contents, or "Scheme of Topics," as the author prefers to call it; on the other hand, the whole book is divided into numbered paragraphs, and it is these latter figures which have been used in both cases for reference.

Having rounded off the first 252 pages, the author skips two and begins again in Part II., called "Experimental Illustrations," with a fresh series of page and paragraph numbers from one onwards, extending to p. 106; but, on p. 90 the paragraph numbers stop at 601, to be resumed on p. 91 at 1 again; they then continue to the end, where they reach par. 23.

When we further add that the second part is included in the index in the middle of the volume, it may perhaps be conceived what a tangle the whole thing is in.

In spite of a certain amount of merit in the descriptions and general language used, we are sorry we cannot recommend this book. The two parts should have been intelligently combined into a homogeneous whole; in its present shape, the student would be half his time turning from the index in the middle to one or the other ends, if he was really anxious to follow that excellent rule of letting theory go hand in hand with practice.

CORRESPONDENCE.

VOLUMETRIC ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—Mr. Ramage's conclusion "that the rare metals now used in the manufacture of certain special steels do not interfere when present only in small quantities," hardly does justice to the account we gave of the influence of these metals when present in such amounts as the Sheffield steel manufacturers think it desirable to introduce. We said nothing about their being present only in small quantities; in fact, in their alloys they are neces-

sarily present in large quantities, and both then and otherwise some of them *do* interfere with the manganese estimation, if the final titration is made with hydrogen peroxide.

It is true that the only point dealt with in our private correspondence with Mr. Ramage was whether the correct result was obtained by filtering the permanganate into hydrogen peroxide or by filtering into an empty flask. The correspondence originated by our communicating the observation that when the permanganate was filtered into peroxide, the results obtained were higher than when it was filtered into an empty flask and peroxide added afterwards. Mr. Ramage's criticism of our paper compels us to state that he at first refused to credit this, and assured us that he preferred the same mode of working for steels as for spiegels, &c., and practised it. We are sorry to remind him of this, as well as of the fact that some time later he admitted the difference, and, as he says, sent one of us a report which purported to explain it.

We are surprised to find that Mr. Ramage refers to this report at all, because it failed hopelessly to elucidate the cause of the differing results. Mr. Ramage had maintained, and the report alluded to attempted to prove—by comparison of results with what we suppose were absolute standards and otherwise—that it was correct to filter into an excess of hydrogen peroxide. On the contrary, we were experimentally satisfied that it was better to filter into an empty flask. Mr. Ramage's first paper justified our position by advocating this procedure.

We do not contend that the *intended* point of the footnote in the *Trans. Chem. Soc.*, 1895, 275, was well hit off by our reference to it, but the matter of fact of the footnote, which so largely influences Reddrop and Ramage's deductions in their Chemical Society's paper, was nevertheless truly represented. They say in effect that the nitric acid solution of ferric nitrate decomposes permanganate more readily than it does hydrogen peroxide, and they argue from this that "all the results obtained by Schneider's method will be below the truth," because Schneider filters into an empty flask instead of into an excess of peroxide as they do in the assay of rich manganese alloys. Now, in Mr. Ramage's paper (CHEMICAL NEWS, vol. lxxxiv., p. 209), he admits that for each c.c. of decinormal hydrogen peroxide added to a solution containing 1.1 grms. of steel or iron in nitric acid, about 0.1 c.c. is at once reduced; that is to say, the hydrogen peroxide is decomposed by the ferric nitrate much more readily and extensively than permanganate could be, which is certainly contrary to the statement of the footnote referred to.

No question of inaccuracy has, as Mr. Ramage says (CHEMICAL NEWS, lxxxiv., 209), been raised regarding the results obtained in the analysis of ferromanganese and spiegel. But unless he can show that the reaction between acid solutions of ferric nitrate and hydrogen peroxide ceases when several times less than 1.1 grms. of iron and much manganese are present, the said question of inaccuracy certainly ought to be raised and settled. For it appears to us at any rate possible, that the 0.6 per cent difference which was found by Reddrop and Ramage between the results of assays of an 80 per cent ferromanganese by their mode of procedure and Schneider's, may actually measure the deficiencies of their mode and not those of Schneider's.

The rest of our differences with Mr. Ramage are either matters of opinion which do not materially interfere with the working of the process either way, or they are such points as interested persons may settle for themselves by a few simple experiments.

We adhere most strongly to ferrous ammonium sulphate in preference to hydrogen peroxide. We quoted no test analyses in support of this modification because we consider them to be unnecessary. But for a considerable time an abundance of tests has been accumulated from at least a dozen sources; we will oblige Mr. Ramage with one of many similar series of determinations as evidence of our desire to ascertain the truth.

Mode of estimating the manganese.	Resulting percentage Mn.		
	I. Carbon, 1'12 per cent.	II. Carbon, 0'34 per cent.	III. Carbon, 2'25 per cent.
1. Gravimetric estimation of the Mn	0'32	1'03	0'92
2. Bismuthate—Filtration into empty flask	0'32	1'00	0'84
3. Bismuthate—Filtration into excess H ₂ O ₂	0'36	1'10	0'95
4. Organic matter destroyed in hot solution with bismuthate, filtration into empty flask, and titration with ferrous sulphate . .	0'31	1'01	0'89
5. As in 4—Filtration into excess ferrous sulphate	0'30	1'01	0'88
6. Acetate separation of iron—Filtrate precipitated with Br and AmHO. Precipitate ignited, dissolved in HCl, evaporated with H ₂ SO ₄ , and finished by oxidation with bismuthate and titration with H ₂ O ₂ . .	0'32	1'02	0'90

—We are, &c.,

FRED. IBBOTSON.
HARRY BREARLEY.

Bower Road, Sheffield.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—If, as a consequence of the voting upon Professor Frankland's motion at last Thursday's Extraordinary General Meeting of the Chemical Society, the day and hour of meeting of the Society are to be changed to 5.30 p. m. on Wednesday, as arranged by the Council, it will be most unfortunate for all who are in positions similar to ours; and they are not a few, and are rapidly increasing in number.

We are engaged in research work of a technical character in a factory some 10 miles from Burlington House, and as our working day is not done till 6 o'clock we cannot possibly attend a meeting at 5.30 p.m.; indeed, it has always been as much as we could manage conveniently to be there by 8 o'clock.

We have, however, been regular attendants; one of us for over four years.

Mr. Howard stated at Thursday's meeting that it would be more convenient for him and his brothers to have the hour changed to 5.30 p.m., and that every facility would be given to their chemists to attend at that hour. But, in the first place, Mr. Howard's attitude is not at all representative of the views taken by employers, many of whom are not chemists, and do not appreciate the necessity for keeping in touch with modern thought; and, secondly, a chemist worth his salt and engaged in research work does not wish to leave his work untouched for an afternoon every fortnight, nor would he do so even if his employer gave consent.

We wish to emphasise the fact that there is a growing number of chemists, working in or near London, who are in the position of having, more or less, to justify their appointment by producing results, and effecting improvements in commercial processes.

These men want and deserve encouragement, and do not wish to be denied those privileges of discussing problems and getting new ideas which they have hitherto enjoyed through the Chemical Society. They will not leave their work to attend meetings at 5.30 p.m. except very occasionally.

It is admitted by all parties that the expression of opinion by the Fellows, per the original postcard, is not what would be given now that the position is more clearly understood. Further, it is obvious, and was admitted by

Professor Smithells on Thursday, that the country members are, with rare exceptions, quite indifferent to the day and hour of meeting; they would not come in appreciably larger numbers than they do, no matter when the meetings were held.

At the same time there could be, we imagine, no objection on the part of the London Fellows to an occasional meeting at 5.30 p.m., as Professor Ramsay suggested, for the sake of the Country Fellows, if they so desired; and no doubt the London Fellows would make special efforts to attend on such occasions in order to meet old friends.

We desire, in conclusion, to express our thanks to those gentlemen who have done so much to represent the position in this matter of that class of chemists to which we belong.—We are, &c.,

TWO FACTORY RESEARCH CHEMISTS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 22, November 25, 1901.

Compounds of Aluminium Chloride with the Alkaline Chlorides.—E. Baud.—Amongst the spinel chlorine compounds are found the following mixed chlorides:— $\text{Al}_2\text{Cl}_6 \cdot 3\text{NaCl}$ and $\text{Al}_2\text{Cl}_6 \cdot 3\text{KCl}$; also, very probably, the chlorated cryoliths $\text{Al}_2\text{Cl}_6 \cdot 6\text{NaCl}$ and $\text{Al}_2\text{Cl}_6 \cdot 6\text{KCl}$. Even these latter bodies do not apparently represent the limiting compounds of Al_2Cl_6 with the alkaline chlorides, but it is difficult to establish thermometrically the existence and the exact composition of the higher ones, on account of the very small proportion of heat evolved during the fixation of the last molecules of the alkaline chlorides.

Preparation of Barium.—M. Guntz.—Pure barium has never been obtained up to the present time. The author finds, however, that, during certain experiments on the stability of barium amalgam, he obtains the metal in a pure state and is able to study its properties. The barium amalgam is obtained very easily and in considerable quantity by the electrolysis of a saturated solution of BaCl_2 , the cathode being made of mercury and the anode of an alloy of platinum and iridium. A 3 per cent amalgam of barium is obtained, from which the barium is prepared by distilling off the mercury in a vacuum at a bright red heat. Barium in a metallic state is a silver white metal, as soft as lead. It fuses at a dull red heat, and is very volatile at bright red heat. It rapidly oxidises in the air, giving baryta in the form of a condensed powder.

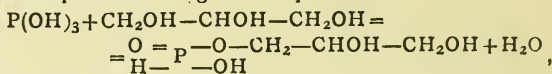
A New Volatile Salt of Beryllium.—G. Urbain and H. Lacombe.—When beryllium hydrate is dissolved in dilute acetic acid and the whole evaporated over the water-bath, a gummy mass is obtained; this substance presents none of the characteristics of a definite compound. If, however, this mass is treated with crystalline acetic acid at boiling-point, a solution is obtained which, on cooling, deposits first needle-shaped crystals, and, at a lower temperature, small octahedral crystals. The molecular weight and analysis of this crystalline compound show it to have the formula $[\text{CH}_3\text{CO}_2]_6\text{Be}_4\text{O} = 406$, admitting $\text{Be} = 9$ and $\text{BeO} = 25$. It is impossible to reconcile the composition of the body and density of the body by supposing $\text{Be} = 13.5$ and $\text{Be}_2\text{O}_3 = 77$. This new compound affords, therefore, a new argument in favour of the diatomicity of beryllium. The authors are continuing their researches on this subject.

Action of Fuming Sulphuric Acid on Ethylic and Propylic Aldehydes and Acetone.—Marcel De'épine.—The author's researches on the action of fuming sulphuric acid on ethylic and propylic aldehydes and acetone show that these aldehydes and acetone, which are acted upon by ordinary strong sulphuric acid, react in a more definite manner with the fuming acid. In fact, these compounds fix a certain number of molecules of SO_3 , giving rise to stable salts of the acid when in acid or neutral media, but salts which are very easily changed by alkalis; these latter breaking the carbon chain in two places.

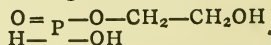
Electrolytic Preparation of the Halogen Compounds of Acetones.—A. Richard.—If an electric current traverses a mixture of hydrochloric acid and acetone, at the end of an indefinite period a dark liquid is obtained which attacks the eyes; this liquid is monochloroacetone, $\text{CH}_3\text{—CO—CH}_2\text{Cl}$. An analogous reaction occurs if an electric current passes through a mixture of hydrobromic acid and acetone. In this case it is monobromoacetone, $\text{CH}_3\text{—CO—CH}_2\text{Br}$, which is produced. These two reactions have been noticed by several chemists, but have not been the object of systematic research. The author therefore undertakes this investigation, examining the conditions of preparation, purification, and principal reactions of the two halogen acetones.

Transformation of two Xanthidrols into Xanthenes by a New Reaction.—R. Fosse.—The author's researches were carried out on dinaphthoxanthidrol and xanthidrol; his experiments on their transformation into xantheoses lead him to the following conclusions:—1. The mono-halogen derivatives of the xanthene series obtained either by the action of the halogens on the xanthenes or by the action of the fuming hydric acids on the xanthidrols behave as basic salts and give double salts with several alkaloid reagents. (2). These same bodies react on alcohol in the same manner as diazoic salts; they form the corresponding carbide, transforming alcohol into aldehyde and giving the hydracid.

Etherification of Phosphorous Acid by Glycerin and Glycol.—P. Carré.—If equimolecular proportions of glycerin and phosphorous acid are heated together, a certain proportion of the acid is etherified—the proportion varying with the conditions of the experiment. From the actions of the phosphoric acid on litmus solution and phenolphthalein, the author concludes that the reaction takes place according to the equation—



and that the glycerophosphorous acid formed is monobasic to litmus and to phenolphthalein. This property enables him to estimate the etherification by simple volumetric titrations. The reaction of glycol is comparable with that of glycerin, furnishing the acid,—



The barium salt of this acid is also prepared; its formula, $\text{P}_2\text{O}_3\text{H}_{12}\text{C}_4\text{Ba}$, being established by analysis.

MEETINGS FOR THE WEEK.

SATURDAY, 28th.—Royal Institution, 3. (Christmas Lectures to Young People). "On Waves and Ripples in Water, Air, and Ether," by Professor J. A. Fleming, M.A., F.R.S., D.Sc.

ST. PAUL'S SCHOOL.—An Examination will be held at St. Paul's School, West Kensington, on Tuesday, January 14th, 1902, and following days, for filling up about Four Vacancies on the Foundation.—Full particulars can be obtained from the Bursar.

THE CHEMICAL NEWS.

VOL. LXXXIV., No. 2196.

ON THE MUTUAL ACTION OF ALUMINA AND FERRIC OXIDE AT INCIPIENT WHITE HEAT.

By H. WARTH, D.Sc.

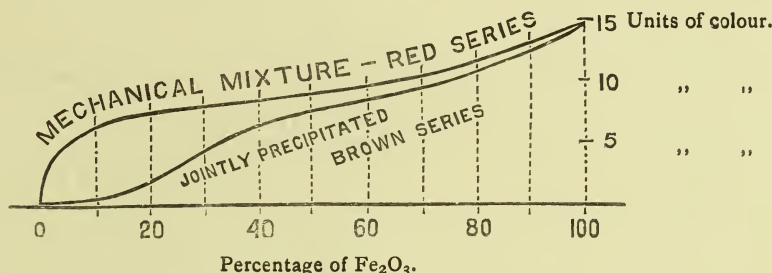
Late Deputy Superintendent Geological Survey of India.

DURING an examination of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) from the Madras Presidency, possessing a pale reddish colour due to ferric oxide, I was much struck by the manner in which the mineral turned perfectly white when heated over the blowpipe flame, and decided to inquire into the cause of the phenomenon.

The decoloration in question is mentioned by Dana, who suggests, however, no explanation of it.

One of the first experiments I made was the following:—Ammonia was added to a solution containing aluminic and ferric salt in such proportion that the precipitate,

DIAGRAM SHOWING THE DEGREES OF COLOUR ESTIMATED FOR THE RED AND BROWN MIXTURES OF Fe_2O_3 AND Al_2O_3 .



after expelling the water, contained exactly 1 per cent. of Fe_2O_3 . This mixed precipitate, after heating over a Bunsen flame, was much less coloured than the gibbsite just alluded to, and on heating it over the blowpipe flame it became pure white. I now treated this white product after pulverisation with ferric salt and ammonia in such a way that it became coated, as it were, with ferric oxide, the latter amounting to 0.5 per cent of the whole, and after heating gently over the Bunsen flame it had imparted a good red colouring very similar to that of the natural gibbsite, only stronger. I estimated the depth of tint as equal to three units of colour, a unit having been arbitrarily chosen in the shape of a rather red sample of gibbsite. Heating this powder, which had 3 units of colour, over the blowpipe flame rendered it snow white. A second treatment, adding 1 per cent more Fe_2O_3 , had a similar effect, leaving the sample containing in the aggregate 2.5 per cent Fe_2O_3 , with a brownish white tint equal by guess to 0.1 of my assumed unit of colour.

It was thus proved that alumina had the property of nearly completely decolorising red oxide of iron at the temperature of the blowpipe flame, and there remained no doubt that the gibbsite owes its decoloration before the blowpipe to this property of the alumina. I also added some pure dry ferric oxide to some whitened gibbsite in the proportion of 1 per cent, which made the sample pink, say about 2 units, and on heating over the blowpipe flame, this colour almost entirely disappeared, thus again showing that the dry substances react by a kind of cementation process at the temperature of the blowpipe flame.

In the next step of this enquiry I gradually increased the proportion of ferric oxide in the mixed precipitate, and I found the decoloration to continue up to 7 per cent Fe_2O_3 , but beyond this there was a slowly increasing brown tint, which was well pronounced when 18 per cent of Fe_2O_3 had been reached. This brown colour continued to 34 per cent Fe_2O_3 without any admixture of red. Beyond this at 60 per cent and 75 per cent there was a darker brown with perhaps a tinge of red, but it was clear that throughout I had to deal with a series of various shades of brown. I have attempted to represent the series by a diagram, but I would mention that this diagram is merely based on ocular estimation.

The ignition was at first effected in a platinum crucible, but thin layers of the mixtures in contact with the walls of the crucible were sometimes altered, probably owing to the passage of hydrogen through the platinum. I therefore continued the tests in a porcelain crucible at the highest attainable temperatures.

The state of oxidation of the iron in the ignited samples was next tested by using for this purpose the precipitates with 5, 8, and 34 per cent of Fe_2O_3 . I dissolved by means of boiling sulphuric acid, and added solutions of potassium ferro- and ferricyanide, which proved unmistakably that only ferric and no ferrous oxide was present in all cases. A trial was also made by that delicate magnetic method

of weighing with and without magnet beneath the pan which General McMahon has introduced, which showed the absence of magnetic oxide (Fe_3O_4), so that we clearly have to do with a combination of Al_2O_3 and Fe_2O_3 only.

All the above-mentioned mixtures of simultaneously precipitated Fe_2O_3 and Al_2O_3 which had been ignited over the blowpipe flame were of a brownish tint, and quite different in colour from an unignited mixture of pure anhydrous Fe_2O_3 and pure anhydrous Al_2O_3 . The latter mechanical mixtures are all red and the amount of tint is shown by a curve in the above-mentioned diagram. The red series shows a rapidly rising curve. The two curves (for the red and the brown series), are widely divergent when the percentages of Fe_2O_3 are low; the one is convex while the other is concave. The colouring of the red series is very strong in comparison with that of the brown series. There is undeniable decolorisation in the case of the latter.

This behaviour of alumina with ferric oxide may be compared with the well-known cobalt-nitrate blowpipe test. The beautiful colour obtained in the latter reaction may also be produced from the solid oxides without the application of any solvent, and it seems that some kind of cementation of the solid substances takes place at the temperature of the blowpipe flame. Fresenius ("Qualitative Analysis," 10th ed., p. 105), says the blue substance is "a compound of the two oxides."

As already mentioned, dry ferric oxide mechanically mixed with alumina in the proportion of 1 per cent likewise became decolorised at the temperature of the blowpipe flame. This experiment was subsequently repeated

with larger proportions, and with some care a mixture containing as much as 34 per cent of red ferric oxide acquired a brown tint very similar to the 34 per cent sample of the brown series obtained from the jointly precipitated oxides.

It is a remarkable circumstance that ferric oxide by itself has at the temperature of the blowpipe flame already a decided tendency to change into magnetic oxide (which it does entirely at a full white heat), and that this tendency is checked by the presence of alumina, as is undoubtedly demonstrated by the above experiments.

But more than this, a mixture of alumina with 6·8 per cent of finely pulverised magnetic oxide (Fe_3O_4) after careful ignition also acquired a brown tint, and was finally found free from ferrous oxide, the iron being entirely ferric. The contact with alumina at the temperature of the blowpipe flame had thus induced the Fe_3O_4 to take up more oxygen and to be changed into Fe_2O_3 . The above experiments thus seem to indicate that the molecules of iron are enabled by the presence of alumina to combine with a larger proportion of oxygen than if left to themselves.

As regards the change of colour of the mixtures from red to brown, this need not imply a chemical combination between the Fe_2O_3 and Al_2O_3 . We are familiar enough with changes of colour when differently coloured metals form, for instance, alloys such as brass, and it appears also possible that two oxides which are so decidedly isomorphous as Fe_2O_3 and Al_2O_3 may diffuse into each other with change of colour without their forming a compound.

VOLUMETRIC DETERMINATION OF ALUMINA FOR TECHNICAL PURPOSES.

By C. R. GYZANDER.

(Concluded from p. 297).

Determination of Basic Alumina.

To 50 c.c. each of the alum solutions before mentioned were added 0·6 c.c. standard soda solution, equivalent to 0·6 per cent Al_2O_3 .

Two c.c. standard sulphuric acid were next added, and the whole left standing, with occasional stirring, to dissolve the hydrate of alumina thrown out. Two drops methyl indicator and 100 c.c. distilled water were then added and standard soda solution run in, drop by drop and with constant stirring for a few seconds between each drop, until the colour changed to orange. The number of cubic centimetres of standard soda solution used were subtracted from 2, and the remainder expressed per cent basic alumina found. The following results are the average of five determinations:—

	NaOH consumed.	Basic Al_2O_3 found.	Error.
	C.c.	Per cent.	
1.	1·4	0·6	0·0
2.	1·4	0·6	0·0
3.	1·4	0·6	0·0
4.	1·4	0·6	0·0
5.	1·4	0·6	0·0
6.	1·5	0·5	-0·1
7.	1·8	0·2	-0·4
8.	2·0	0·0	-0·6
9.	2·1	0·0	0·0

These results show that the basic alumina was correctly determined in sulphates containing up to 60 per cent $\text{Al}_2(\text{SO}_4)_3$. Above that percentage, the orange point is no longer the correct end-point for neutrality, as this begins to turn more and more towards the red-orange with increase of $\text{Al}_2(\text{SO}_4)_3$. It appears from these tests as if No. 8 was neutral and No. 9 acid, equivalent to 0·1 c.c. standard soda solution, which would be 0·29 per cent H_2SO_4 .

The basic alumina is, however, easily determined, even in such high testing sulphates, if the point of neutrality is compared with a blank made from pure alum and containing the same percentage of $\text{Al}_2(\text{SO}_4)_3$ as the sulphate to be tested. Thus, 50 c.c. each of the alum solutions—from No. 6 to No. 9 inclusive—were treated with 2 drops of methyl indicator and 100 c.c. distilled water, and these served as blank standards with which the titration end-points were compared in another 50 c.c., made basic by the addition of standard soda solution, and the results were in every instance correct.

In testing for total $\text{Al}_2(\text{SO}_4)_3$, it is not immaterial whether the sulphate is originally basic or neutral; because, if the sulphate is basic, and this is not corrected by adding sulphuric acid, then the results will be much too low, as basic salts are thrown down by the caustic solution, whether this be strong or dilute, as the following test will show.

16·6066 grms. of alum were dissolved in about 500 c.c. distilled water, and then made basic by adding 20 c.c. standard soda solution. The alumina at first thrown out dissolved completely upon shaking; the solution was made up to a litre. We have here a solution equivalent to sulphate containing 56·67 per cent $\text{Al}_2(\text{SO}_4)_3$, with 1·0 per cent basic.

Fifty c.c. of this solution, 2 drops methyl, 4 drops phenol indicator, and 100 c.c. distilled water gave, on an average of five determinations, 16·64 per cent Al_2O_3 or 55·41 per cent $\text{Al}_2(\text{SO}_4)_3$, a difference of 1·26 per cent. This is a much greater difference than resulted in testing a 60 per cent neutral sulphate (see No. 5). The dilute standard gave 55·92 per cent $\text{Al}_2(\text{SO}_4)_3$, a difference of 0·75 per cent.

To another 50 c.c. were added 2 c.c. standard sulphuric acid, then indicators and distilled water as before. Standard soda required to orange was 1 c.c., or basic Al_2O_3 is 1 per cent. Continuing the addition of standard soda to permanent pink required, on an average of five determinations, 18·94 c.c. Deducting from these, 2 c.c. acid originally added, leaves 16·94 per cent Al_2O_3 or 56·41 per cent $\text{Al}_2(\text{SO}_4)_3$, which result is practically correct. In like manner, when using dilute standard soda solution, there was required, on an average of five determinations, 63·16 c.c. Deducting the equivalent of 2 c.c. standard acid, or 6·6 c.c. dilute standard, leaves, as final result, 56·56 per cent $\text{Al}_2(\text{SO}_4)_3$.

The influence of temperature on the determination of alumina will be seen from the following. Fifty c.c. alum solution, containing the equivalent of 10 grms. of a 58 per cent sulphate per litre (see No. 4 in table) gave at—

°C.	Per cent Al_2O_3 .
25	17·4
30	17·5
35	17·8
40	18·3
45	18·7
50	19·3

When another 50 c.c. of the same solution, and indicators as before, were heated to 50° C., and 18·5 c.c. of standard soda added, the colour was yellow, due to the methyl-orange, but showed no trace of pink, although 1·06 c.c. excess of alkali had been added. As the solution gradually cooled, the pink colour began to appear, and at 35° C. the colour was intensely red, which shows that alumina is acid to phenolphthalein at high temperatures.

Determination of Free Acid in Sulphate of Alumina.

It has already been mentioned that an increase in $\text{Al}_2(\text{SO}_4)_3$ alters the colour produced by methyl-orange, and the more concentrated the solution is, the more noticeable is this colour change. As commercial sulphates vary from 50 to 58 per cent, the amount of sulphate contained in half a gram. would vary from 0·25 to 0·29 gram. Potash alum containing equivalent quantities of sulphate of alumina would then be 0·6919 and 0·8026 gram.

These quantities were dissolved in 150 c.c. water and 2 drops of methyl indicator added. Comparing the shades produced with that of 0.5 gm. alum in 150 c.c. distilled water and 2 drops methyl indicator, there was a barely perceptible difference between them; that is, one might have called the one containing 0.5 gm. of alum for orange and the others red-orange, but for all practical purposes they were alike. By adding tenth-normal sulphuric acid to the alum solution containing 0.5 gm. in 150 c.c., it was found that 0.2 c.c. gave a barely perceptible red-orange, 0.4 c.c. a distinct red orange, while 1 c.c. was strongly pink coloured. Referring the amount of sulphuric acid added to 0.5 gm. original alum, we find that about 0.2 per cent free acid would be detected with difficulty, while twice the amount or more is readily detected by comparing the colour produced with methyl-orange with that of 0.5 gm. alum in 150 c.c. water. If, therefore, a sulphate, when tested as already described for basic, consumes more than 2 c.c. standard soda to neutral, then the excess must be due to free sulphuric acid in the sulphate. When the excess of standard soda solution required to produce the neutral tint is more than 0.2 c.c., the acidity must already have made itself noticeable by the pink colour produced with the methyl indicator, but when the excess of standard soda required to neutral is trifling, or when the results indicate neutrality, there may be a doubt as to the actual acidity or neutrality of the sulphate, as small differences may be due to experimental errors. For practical purposes, such small differences may be neglected, although there occasionally are cases where it is desirable to be able to say with certainty whether a sulphate is actually normal or not.

An attempt to determine free acid in sulphate of alumina by means of alcohol, whether anhydrous or not, was an absolute failure, as a dissociation of the alum always takes place, whereby free acid and basic salts are formed. The following method, based on the behaviour of sulphate of alumina towards ultramarine, was found to give perfectly satisfactory results. As ultramarines differ in their sensitiveness toward acid, the brand that is the most sensitive will be the best for this test. The one I used was known as "E No. 1" of Heller and Merz Co. of New York. I first made up the following solutions:—

Grms.	C.c.	Per cent.
1. 10 of alum + 2 N/10 H ₂ SO ₄		= 0.1 free H ₂ SO ₄
2. 10 " + 1 " "		= 0.05 " "
3. 10 " "		= neutral " "
4. 10 " + 1 standard soda		= 0.05 basic alumina
5. 10 " + 2 " "		= 0.1 " "

Each was made up to 100 c.c.

0.5 gm. ultramarine were shaken up with 500 c.c. distilled water.

Five small flasks containing 20 c.c. of the above alum solutions (2 grms. original alum) and 10 c.c. ultramarine solution = 0.01 gm., were placed on a hot radiator and each stirred up by gently rotating the flask; this was kept up until no more blue colour was visible when holding the flask against a white paper.

No. 1 was colourless in	4.5 minutes
" 2 " "	6.5 " "
" 3 " "	8.5 " "
" 4 " "	9.0 " "
" 5 " "	9.5 " "

Repetition of the experiment gave practically the same results, as the following figures show:—

No. 1 was colourless in	5 minutes
" 2 " "	7 " "
" 3 " "	8 " "
" 4 " "	9 " "
" 5 " "	9.5 " "

In these two series of tests the ultramarine was added to No. 1 solution first, and then in succession, in

numerical order. Although the measuring of the ultramarine with a pipette was quite rapid, yet some little time elapsed between the first and last addition, and as this might possibly have some influence on the earlier loss of colour in the first samples, the test was repeated, but the order of adding the ultramarine was reversed, so that it was added to No. 5 first and to No. 1 last. The results were as follows:—

No. 1 was colourless in	5 minutes
" 2 " "	7 " "
" 3 " "	8 " "
" 4 " "	10 " "
" 5 " "	10.5 " "

The order of adding the ultramarine had therefore no influence on the results. It is also seen that an increase of acidity of the sulphate of alumina from 0.05 to 0.1 per cent had a marked influence on the decomposition of the ultramarine as compared with normal sulphate. It also shows that an increase of basic alumina, even though only from 0.05 to 0.1 per cent, diminishes the action upon the ultramarine, and that the difference in action between 0.05 per cent free acid and 0.05 per cent basic alumina is very marked. Such small amounts of free acid and basic alumina cannot be detected by titration, but are readily detected by the ultramarine method. In carrying out the test on a doubtful sulphate proceed as follows:—Weigh pure potash alum equivalent to the Al₂(SO₄)₃ in 2 grms. of the sulphate in question in several portions, and make them of known acidity and basicity by adding N/10 acid, and standard soda solution. Weigh also 2 grms. of the sulphate in question, and dissolve them each in 20 c.c. distilled water. Add 10 c.c. ultramarine solution, place on a warm radiator, and note the time each requires to be decolorised. The sample decolorised in the same time as the sulphate in question must be equal to it in composition. A certain sample of sulphate of alumina was found to have the following composition when tested gravimetrically:—

Al ₂ O ₃	= 16.750
SO ₃	= 39.241
FeO	= 0.021
SiO ₂	= 0.009
Insoluble	= 0.430
Na ₂ O	= 0.049
H ₂ O	= 43.500 (by difference)
	100.000

The above is calculated as:—

Al ₂ (SO ₄) ₃	= 55.780
Free H ₂ SO ₄	= 0.153
FeSO ₄	= 0.044
SiO ₂	= 0.009
Insoluble	= 0.430
Na ₂ SO ₄	= 0.112
H ₂ O	= 43.472
	100.000

Tested volumetrically as described the following results were obtained:—

Al ₂ (SO ₄) ₃	= 55.810
Free H ₂ SO ₄	= 0.200
FeSO ₄	= 0.044
Insoluble	= 0.430
H ₂ O, &c.	= 43.516
	100.000

Another chemist tested this same sulphate, and reported 0.4 per cent basic alumina. At the same time he stated

that he had used Beilstein and Grosset's method for determining free acid in alum, and had by that method found 0.25 per cent free acid. This result was, however, rejected, as the gravimetric method was considered to be the correct thing.

Starting from my own determination, 55.81 per cent $\text{Al}_2(\text{SO}_4)_3$, 2 grms. of the sulphate is equivalent to 3.0893 grms. potash alum. If this is made 0.4 per cent basic it would require 2.5 c.c. standard soda solution. But the addition of this amount of standard soda would precipitate alumina equivalent to 0.1151 grm. alum. Alum equivalent to 55.81 per cent $\text{Al}_2(\text{SO}_4)_3$, and made 0.4 per cent basic by addition of standard soda solution, would therefore be $3.0893 + 0.1151 = 3.2044$ grms.

The following five solutions were made:—

Grms.	C.c.	Per cent.
1. 3.0893 alum + 0.6 N/10 H_2SO_4		= 0.1 free acid
2. " " + 0.3 " "		= 0.05 "
3. " " — " "		= neutral "
4. " " + 2.5 standard soda		= 0.4 basic Al_2O_3
5. 2 grms. of the sulphate in question.		

Each was dissolved in 20 c.c. distilled water in an Erlenmeyer flask by the aid of heat, and then cooled down to room temperature; 10 c.c. of the well-shaken ultramarine solution added, and the test carried out as already described.

No. 1 was decolorised in	4 minutes
" 2 " " " "	5 "
" 3 " " " "	6 "
" 4 " " " "	13 "
" 5 " " " "	2 "

As No. 5, or the sulphate in question, was the first to be decolorised, it is evident that it must be more acid than No. 1, which was the next to be decolorised, and could not possibly have been 0.4 per cent basic, as the sulphate No. 4, which had that composition, required thirteen minutes for the decomposition of the ultramarine.

Analysis of Bauxite Sulphate.

As both ferric and ferrous sulphate may be accurately determined in exactly the same manner as alumina, provided they are not present in too large amounts, in which case the end-point is obscured by the strongly coloured precipitate formed, all that is needed is to correct for iron in the results of total sulphates when the remainder is alumina. Proceed, therefore, exactly as stated for hydrate sulphate, but determine the total and ferrous iron in two separate portions of 100 c.c. each, strongly acidified with sulphuric acid. For total iron, add liquid sulphurous acid to reduce any ferric iron to the ferrous state, boil off the excess of SO_2 , cool, and titrate with dilute permanganate solution. Ferrous iron is obtained by titrating the other 100 c.c. direct. Subtracting the ferrous from total iron gives the equivalent of ferric iron. The only precaution needed is to have the permanganate solution dilute, titrate in the cold, and to take the first faint pink colour, lasting about a second, as end-point. The pink colour usually disappears after a little while, due to humus compounds which all Bauxite sulphates contain in varying quantities, or possibly to arsenious acid occasionally also present. These two compounds decompose permanganate only very slowly in the cold, and do therefore not occasion any very great error in the results of the iron determination for technical purposes. The iron is calculated as FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$, as the case may be, and its equivalent of standard soda solution, with reference to 0.5 grm. as well as the basic alumina, deducted from the total alumina found, when the remainder, times 3.33, gives $\text{Al}_2(\text{SO}_4)_3$. The permanganate solution which I use requires 30 c.c. for 0.7 grm. ferrous-ammonium sulphate. The following table shows its equivalent of ferrous and ferric sulphate as well as standard soda solution:—

C.c. Permanganate.	Per cent. FeSO_4 .	NaOH. Correction.	Per cent. $\text{Fe}_2(\text{SO}_4)_3$.	NaOH. Correction.
0.1	0.08	0.019	0.11	0.034
0.2	0.17	0.038	0.22	0.068
0.3	0.25	0.057	0.33	0.102
0.4	0.34	0.076	0.44	0.136
0.5	0.42	0.095	0.56	0.170
0.6	0.51	0.114	0.67	0.204
0.7	0.59	0.133	0.78	0.238
0.8	0.68	0.152	0.89	0.272
0.9	0.76	0.171	1.00	0.306
1.0	0.85	0.190	1.11	0.340
1.1	0.93	0.209	1.22	0.374
1.2	1.02	0.228	1.33	0.408

15.7757 grms. alum were dissolved in 500 c.c. distilled water, and 12 c.c. standard soda solution added. When clear, 0.1828 grm. pure $\text{FeSO}_4 + 7\text{aq.}$ was added, and the whole made up to 1 litre. This gives a solution equivalent to 10 grms. of a sulphate of the following composition:—

	Per cent.
$\text{Al}_2(\text{SO}_4)_3$	55.00
Basic alumina	0.60
FeSO_4	1.00
Water, &c.	43.40
	100.00

Fifty c.c. of this solution, 2 c.c. standard acid, 2 drops methyl indicator, 4 drops phenol indicator, and 100 c.c. distilled water gave for basic alumina 0.7, 0.6, 0.6, 0.5; average, 0.6 per cent. Total sulphates obtained were 17.3, 17.4, 17.4, 17.4; average, 17.38.

One hundred c.c. acidified with sulphuric acid required for ferrous iron 1.2 c.c. permanganate solution, or 1.02 per cent FeSO_4 . 100 c.c. of the solution, strongly acidified with sulphuric acid, 10 c.c. of a 6 per cent SO_2 solution added, the excess of SO_2 boiled off, the solution cooled, and titrated with permanganate, required for total iron 1.2 c.c. as before. There was, therefore, no ferric iron present.

1.02 per cent FeSO_4 corresponds to 0.228 c.c. standard soda solution. Adding this to the 0.6 per cent basic gives a total correction 0.828, which subtracted from 17.38 leaves as remainder 16.552, which multiplied by 3.33 gives 55.12 per cent $\text{Al}_2(\text{SO}_4)_3$. The results were therefore:—

$\text{Al}_2(\text{SO}_4)_3$	55.12
Basic Al_2O_3	0.60
FeSO_4	1.02
Water, &c.	43.26
	100.00

which results are satisfactory.

A commercial Bauxite sulphate gave the following result by gravimetric method:—Insoluble = 0.06, SiO_2 = 0.01, As_2O_5 = 0.03, FeO = 0.04, Fe_2O_3 = 0.27, Al_2O_3 = 17.76, CuO = 0.003, Na_2O = 0.19, H_2O = 41.44, SO_2 = 40.37; total, 100.143 per cent. These results are equivalent to:—

$\text{Al}_2(\text{SO}_4)_3$	56.687
Basic Al_2O_3	0.74
FeSO_4	0.08
$\text{Fe}_2(\text{SO}_4)_3$	0.67
CuSO_4	0.006
Na_2SO_4	0.42
SiO_2	0.01
As_2O_5	0.03
Insoluble	0.06
H_2O	41.44
	100.143

The volumetric determination gave the following result:—Basic alumina 0.85, 0.85, 0.85. Total sulphate 17.95, 17.95, 17.90; average, 17.93.

FeSO₄ .. = 0.08 per cent = 0.019 NaOH correction
Fe₂(SO₄)₃ .. = 0.67 per cent = 0.204 NaOH correction
0.85 basic

1.073 total correction
(17.93 - 1.073) × 3.33 = 56.13 per cent Al₂(SO₄)₃.

Total results:—

Al ₂ (SO ₄) ₃	56.13
Basic alumina	0.85
FeSO ₄	0.08
Fe ₂ (SO ₄) ₃	0.67
Insoluble	0.06
Water, &c.	42.21

100.00

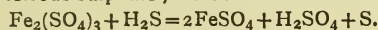
Analysis of Sulphate of Alumina containing Zinc Sulphate.

The sulphuric acid in zinc sulphate cannot, like that in sulphate of iron and alumina, be titrated with standard soda solution in the cold. If the solution, containing only zinc sulphate, is boiling hot, then the results are correct when phenolphthalein is indicator. As sulphate of alumina cannot be tested under these conditions, it follows that a separation of the two is necessary before they can be determined. Zinc can be separated from alumina by means of H₂S in a solution slightly acidified with H₂SO₄, and the ZnS thrown down filters readily if the precipitation is started in a hot solution and continued until cold. The filtered and washed ZnS, after being converted into sulphate or chloride, may be titrated with standard soda solution at a boiling temperature. But another and quicker method is the following:—

When H₂S is led into a solution of ZnSO₄, the following reaction takes place: ZnSO₄ + H₂S = ZnS + H₂SO₄. For every molecule of ZnS formed one molecule of H₂SO₄ is liberated. If, therefore, the free acid formed is determined, the zinc may be calculated from it.

One c.c. standard soda solution is equivalent to 0.02344 gm. ZnSO₄.

Ferric sulphate also liberates sulphuric acid when reduced to ferrous sulphate; thus:—



Basic alumina, if present, will neutralise an equivalent amount of acid, all of which must be borne in mind. The analytical operation will, therefore, be as follows:—Dissolve 10 grms. in distilled water, and filter. Dilute to 1 litre, and mix by shaking. In 50 c.c. determine basic Al₂O₃, and in 100 c.c. each, ferrous and ferric sulphates. To other 50 c.c. add standard sulphuric acid, equivalent to basic alumina present; heat to near boiling, and pass H₂S through until cold. Allow to settle, and filter the solution. If for any reason the solution does not filter clear, return the filtrate until it is clear, then wash the precipitate thoroughly with distilled water containing a little H₂S. Boil the clear filtrate to expel H₂S, and bring the volume down to 150 c.c. if need be. Cool, and determine free acid, after adding 2 drops of methyl indicator, by titration with standard soda solution to orange, then add 4 drops of phenol indicator, and titrate as mentioned for total sulphates, which now includes all the iron as FeSO₄. From the total sulphates found, deduct the standard soda equivalent of total iron as FeSO₄ + basic, and the remainder, times 3.33, is Al₂(SO₄)₃. From the free acid found after precipitation with H₂S, deduct that equivalent to Fe₂(SO₄)₃ (the basic was corrected for by adding standard acid before H₂S treatment), and the remainder is calculated as ZnSO₄.

An artificial aluminium-zinc sulphate was prepared as follows:—15.7757 grms. pure potash alum were dissolved in 500 c.c. distilled water, and 12 c.c. standard soda added. When clear 0.1828 gm. FeSO₄ + 7aq. and 0.8913 gm. ZnSO₄ + 7aq. were added. Another 0.1828 gm. FeSO₄ + 7aq. and 2.25 c.c. standard sulphuric acid were oxidised with nitric acid in platinum dish to dryness on the water-bath, then dissolved in water, and the solution added to the

previous mixture, which was diluted to 1 litre, and thoroughly mixed by shaking. This gave a solution equivalent to 10 grms. of a sulphate of the following composition:—

	Per cent.
Al ₂ (SO ₄) ₃	55.00
Basic Al ₂ O ₃	0.60
FeSO ₄	1.00
Fe ₂ (SO ₄) ₃	1.32
ZnSO ₄	5.00
Water, &c.	37.08
	100.00

Fifty c.c. of this solution, 2 drops methyl indicator, and 100 c.c. water gave for basic alumina 0.6 per cent.

100 c.c., acidified with sulphuric acid, required 1.2 c.c. permanganate solution = 1.02 per cent FeSO₄.

100 c.c. + 10 c.c. 6 per cent SO₂ solution + 10 c.c. concentrated sulphuric acid, boiled until free from SO₂, cooled, and diluted, required 2.4 c.c. permanganate solution for total iron. Deducting 1.2 c.c., due to FeSO₄, leaves 1.2 c.c. as Fe₂(SO₄)₃ = 1.33 per cent.

Fifty c.c. of the solution + 0.6 c.c. were heated to near boiling, then H₂S passed through until cold, the solution left to settle, after which it was filtered, and the precipitate washed thoroughly with freshly prepared and very dilute H₂S water. The clear filtrate was boiled to expel H₂S, cooled, diluted to 150 c.c., 2 drops of methyl indicator added, and the free acid titrated with standard soda solution to orange. Three determinations required 1.25, 1.20, 1.20 c.c.; average, 1.21. This includes acidity due to ferric sulphate, which is equivalent to—

$$\frac{0.132}{400} \times \frac{1}{0.01427} \times \frac{50}{100} = 0.11 \text{ c.c.}$$

standard soda solution, which when subtracted from 1.21 leaves 1.10 c.c. due to ZnSO₄, and corresponds to—

$$1.10 \times 0.02344 \times \frac{100}{50} = 5.17 \text{ per cent ZnSO}_4.$$

After determining free acid 4 drops of phenol indicator were added, and the titration continued to permanent pink. It required 17.6, 17.5, 17.7 c.c. standard soda solution, or, on an average, 17.6 c.c. This includes basic alumina and total iron as FeSO₄, which is equivalent to 0.456 c.c. standard soda solution for the iron, and 0.6 c.c. for the basic alumina, or a total of 1.056 to be deducted from 17.6, which leaves 16.544. This multiplied by 3.33 gives 55.09 per cent Al₂(SO₄)₃.

Total results:—

Al ₂ (SO ₄) ₃	55.09
Basic alumina	0.60
FeSO ₄	1.02
Fe ₂ (SO ₄) ₃	1.33
ZnSO ₄	5.17
Water, &c.	46.79

100.00

A sulphate of similar composition must not be allowed to stand for any length of time after being made up to a litre, as, on account of the high percentage of iron, insoluble basic ferric sulphates are thrown down, with liberation of sulphuric acid, which will react with the basic alumina and thus make the results too low. Sulphates with such high percentage of iron are hardly ever met with in practice, but was purposely added to this sample in order to show what could be done under such conditions. Should there be less than 5 per cent ZnSO₄ in the sulphate, more than 50 c.c. of the solution will be required for precipitation with H₂S, in order to bring the free acid up to a determinable quantity. In that case, the methyl end-point should be compared with a blank, made from pure potash alum and containing approximately the same amount of Al₂(SO₄)₃ in an equal volume of water. After determining free acid, a portion equal to

50 c.c. of the original solution should be tested for total sulphates.

The standard soda solution was standardised at 20° C., and the contraction and expansion between 12° and 30° C. were determined by observing the specific gravity between these temperatures. It was thus found that potash alum, which at 20° should test 10·85 per cent $\text{Al}_2(\text{SO}_4)_3$, would at 12° test 10·83 per cent, and at 30° test 10·87. These variations do not affect the results, as they are less than the probable experimental error.

Another matter which must be borne in mind is that the rate of delivery of standard soda solution must be the same at all times when testing for total sulphates, or the results will vary quite considerably. The slower the delivery, the less standard soda solution will be required to produce the end-point with phenolphthalein. The rate of delivery should therefore be the same as that maintained in standardising the solution against the acid sodium oxalate. A rapid succession of drops is preferable to a full stream. This matter is, of course, not peculiar to this method, but applies to all volumetric work, and is due to the fact that the burette does not recover perfectly; that is to say, the liquid adhering to the sides after a rapid delivery is greater than after a slow one, and will not run down completely, even after several minutes standing, in a burette perfectly clean and free from grease. The necessity for a very slow delivery, when testing for basic, with methyl orange as indicator, must be obvious, as that indicator, in the presence of sulphate of alumina, is by no means instantaneous in its changes. The inaccuracy, due to the delivery, is in that case too small to be noticeable, on account of the small amount of liquid used.

Errors, which usually affect ordinary technical gravimetric alumina determinations, such as neglect to separate silica and metals precipitable by H_2S before precipitating the alumina, and the introduction of silica and alkali from the glass beaker in which the precipitation, as a rule, is made, has no influence on the volumetric determination, and I am convinced, from several years' experience with the method, that the results it gives are much to be preferred to ordinary gravimetric determinations, both as to accuracy and rapidity of execution. Perfectly correct results have been obtained with this method by persons without any analytical training and who could not possibly have made a gravimetric determination.

The ease with which one can accurately determine whether a sulphate is basic, acid, or neutral (normal) will be appreciated by all who for that purpose have had to go through a lengthy gravimetric method.

A NEW CRYSTALLISED SALICYLATE OF BISMUTH.

By PAUL THIBAUT.

WE have already described (*Bull. Soc. Chim.*, February, 1901) a method for preparing hydrated oxide of bismuth by means of which this body can be obtained in a state of purity, and, consequently, able to give pure derived salts by the direct union with acids, among others, salicylate of bismuth.

MM. Wolff (*Journ. de Pharm. et de Chim.*, 1884, p. 123), Jaillet and Ragoucy (*Ibid.*, 1884, p. 113), and Causse (*Bull. Soc. Chim.*, 1891, vol. vi., p. 842), have all given different methods for obtaining salicylate of bismuth, either neutral or basic.

With the exception of M. Causse the above writers took nitrate of bismuth, which they treated in aqueous or glycerinated solution with salicylate of soda. Under the conditions described by these authors we have obtained precipitates which in our experiments always contained a constant appreciable amount of nitric acid, about 6 per cent.

M. Causse, in a very ingenious manner, prevented the precipitation of the oxychloride of bismuth by means of a saturated solution of chloride of sodium; he then added a solution of salicylate of soda, rendered alkaline by the addition of caustic soda. The crystalline precipitate we obtained on repeating this experiment contained considerable quantities of chloride, even after ten washings in water containing a little nitric acid. By still further washing we were able to rid the precipitate of all trace of chlorine, but it had then lost its crystalline appearance, and given up all its salicylic acid.

As a matter of fact, all these products are very unstable, and, as M. Thabuis has remarked (*Moniteur Scientifique*, 1895, p. 9), they resist neither the action of water nor alcohol, or even a temperature of 50° C. Further, the analyses of M. Duyck show ("Sur quelques nouveaux médicaments à base de bismuth") that the proportions of mineral oxide and of organic acid contained in the commercial products are extremely variable.

We have not been able to obtain a neutral or basic salicylate of bismuth in a state of purity.

Researches which we have carried out have led us to replace the hydrated oxide of bismuth by the anhydrous oxide obtained in the ordinary manner.

When we mix together either pure or impure hydrated oxide of bismuth with salicylic acid, even in large excess, either cold or at the temperature of the water-bath, we obtain a non-homogeneous product containing both oxide and organic acid uncombined, and some small transparent crystals which resist the action of alcohol.

On the other hand, by using the anhydrous oxide, the whole of it goes into combination at the temperature of the water-bath.

We finally decided on the following method:—15 grms. of crystallised nitrate of bismuth are precipitated in nitric solution by an excess of caustic soda or potash. After boiling, the whole of the amorphous, white, hydrated oxide is transformed into yellow crystallised anhydrous oxide; it is then thoroughly washed, and 10 grms. of salicylic acid rubbed up with 200 c.c. of water are added. The whole is then left on the water-bath for some time; the reaction is a fairly long one to complete, on account of the insolubility of the compound and of its constituents. When at last it is terminated, which can be decided by making sure by means of the microscope that there are no more opaque, yellow needles of anhydrous oxide left, it is decanted hot, thoroughly washed with cold alcohol, and dried in the oven.

In this manner we obtain a very well crystallised salicylate of bismuth, answering to the formula $(\text{C}_7\text{H}_5\text{O}_3)_3\text{Bi}_2\text{O}_3$.

Analyses gave:—

	Found.			Calculated for, $(\text{C}_7\text{H}_5\text{O}_3)_3\text{Bi}_2\text{O}_3$.
C	28·39,	28·30,	28·37	28·70
H	1·88,	1·85,	1·90	2·05
Bi	46·60,	46·61,	46·76	47·38
O (by difference)	23·13,	22·94,	22·97	21·87

This substance occurs in the form of a dirty-rose coloured powder, distinctly crystallised in small transparent prisms, acting on polarised light. Water decomposes it slowly in the cold, and more rapidly when hot; water saturated with salicylic acid is without action; cold alcohol also has no action, but when warmed it removes the salicylic acid.

Ether, again, is without action, as is also heat up to a temperature of 140°. If we then continue to apply heat the substance melts with decomposition, becoming black, and giving off phenol. Acids, both hot and cold, separate the salicylic acid, giving the corresponding bismuth salt; the alkalis, potash, soda, and ammonia unite with the salicylic acid, leaving the whole of the bismuth as oxide.

To sum up, we have succeeded in obtaining in a very simple manner by replacing the hydrated oxide of bismuth by the anhydrous oxide, a very well crystallised salicylate

of bismuth answering to the formula $(C_7H_6O_3)_3Bi_2O_3$, undecomposable by cold alcohol, ether, or a temperature of 140° , and acting as a true salt of bismuth.

It is, as a matter of fact, as well to make a difference between the true salts of bismuth, which on contact with the alkalis part with the whole of their metallic oxides, and other compounds, wrongly called salts, which are completely soluble in the alkalis. We are following up the examination of these different compounds.—*Bull. Soc. Chim.*, Series 3, vol., xxv., No. 16.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1901.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, December 10th, 1901.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 202 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 202 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford has been again considerably below the average; the actual rainfall measured was 0.54 inch, the average is 2.30 inches; this leaves the serious deficiency of 1.76 inches, and, added to the previous deficit of 2.50 inches, makes a total deficiency for the year of 4.26 inches, or 18.4 per cent on the thirty-five years' average.

Our bacteriological examinations of 534 samples have given the results recorded in the following table; we have also examined 38 other samples, from special wells, standpipes, &c., making a total of 572 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	280
New River, filtered (mean of 126 samples) ..	10
Thames, unfiltered (mean of 26 samples) ..	1909
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 292 samples)	25
Ditto ditto highest	300
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	202
River Lea, from the East London Company's clear-water wells (mean of 38 samples) ..	13

Of the 456 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 20 samples, or 4.3 per cent, were sterile. Four samples contained more than 150 microbes, while only fourteen samples, or 3.0 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the

fourteen excess samples was 154, against a corresponding mean of 149 in seven excess samples during October.

We may point out that although the amount of rain registered at Oxford is far below the average, such has not been the case with regard to the upper gathering grounds of the Thames Valley. There has been, on the contrary, a considerable amount of rain, though not officially measured, only a few miles above Oxford, and it is the fact that the Thames was in flood, and had overflowed its banks for some miles, towards the end of the month. On the other hand, we are informed that there has only been 0.5 inch of rain during the past eight weeks in the valley of the Lea. The general character of the supply during the month has been decidedly above the average, both chemically and bacteriologically, for the time of year.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

By W. F. HILLEBRAND.

DUNNINGTON (*Journ. Am. Chem. Soc.*, vol. xiii., p. 210), has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanous to meta-titanous acid, which does not afford a yellow colour with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and after a time it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow colour in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to an already peroxidised titanium solution weakens the colour. For this reason it is necessary to take the greatest care to ensure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the colour even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the "Technology Quarterly," v. 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralising with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odour of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only 2 or 3 cubic centimetres of the peroxide are employed.—*Bulletin of the United States Geographical Survey*, No. 167.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.

By F. W. CLARKE.

THAT pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers Brothers published a series of observations upon this subject (*Amer. Journ. Sci.*, Series 2, vol. v., p. 401), and showed that some species of minerals would give an alkaline reaction to test-paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows:—A series of glass-stoppered bottles was placed against a white background. In each bottle half a grm. of finely pulverised mineral was put, and then 50 c.c. of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the twenty-two samples examined were treated exactly alike. Two of the bottles were filled with the water, and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remain colourless during the two weeks through which the experiments lasted. The results obtained were as follows:—

Muscovite.—A doubtful trace of coloration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar non-fluoriferous variety from Edwards, New York. Gave a very distinct, permanent pink coloration.

Orthoclase.—A trace of coloration which increased for a few days, and then faded.

Oligoclase.—The transparent variety from Baskerville, North Carolina. Distinct and permanent, but pale coloration.

Albite.—From Amelia County, Virginia. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elæolite from Litchfield, Maine. Good coloration, but partly fading in time.

Cancrinite.—Litchfield, Maine. Gives a deep rose coloration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose colour.

Spodumene.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, New York. Gave a faint, evanescent trace of coloration.

Laumontite.—A doubtful trace of coloration.

Stilbite.—Faint, evanescent coloration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time.

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong coloration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose colour.

Apophyllite.—From Bergen Hill. A very deep rose colour.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light, but in certain cases the coloured solution separated

into two layers, the colour being wholly in the lower. Here the colour was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Toward the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction, and a fairly deep rose colour.

A neat method of demonstrating the reactions described above is the following:—Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orthoclase gave no coloration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite, gave immediately a deep, rich, rose colour. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general the order of intensity of the colour produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase feldspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analysed in the laboratory of the United States Geological Survey was placed in a row of bottles, and treated, just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole-gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite-basalt, felspar-basalt, and diorite gave faint traces of colour. Granite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colorations.

In all of these instances the production of colour is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite, the reaction is striking enough to be used as a lecture-table experiment.—*Bulletin of the United States Geological Survey*, No 167.

THE QUANTITATIVE DETERMINATION OF CADMIUM.*

By EDMUND H. MILLER and ROBERT W. PAGE.

THE work described in this paper was suggested by the difficulties encountered in some experiments on the determination of cadmium, which were undertaken before analysing a number of precipitates of cadmium ferrocyanide. The methods compared are the electrolytic, the carbonate, and the phosphate. The work was done on a solution of cadmium chloride, found to be free from impurities, which after thorough mixing was sealed up in a number of bottles to avoid evaporation.

Electrolytic Determination.

The cyanide method (Riban, "Analyse Chimique Quantitative par Electrolyse," Paris, 1899; Rimbach, *Zeit. f. Anal. Chem.*, 1898, xxxvii., p. 284), was used under the following conditions:—Thirty c.c. of the cadmium chloride solution were diluted to 150 c.c. and 1

* Contribution from the Havemeyer Laboratories of Columbia University. From the *School of Mines Quarterly*, xxii., No. 4.

no free acid, and no excess of ammonium salt beyond the quantity indicated, while that amount is necessary."

A series of determinations was made following Austin's directions as closely as possible; the results were invariably low, and on testing the filtrate with hydrogen sulphide a heavy precipitate of cadmium sulphide was always obtained. (See Table II.)

Instead of experimenting further with Austin's conditions, a more promising field seemed to be the adaptation of the conditions given by Dakin (*Zeit. für Anal. Chem.*, 1900, 39, 273), for the precipitation of zinc ammonium phosphate to the determination of cadmium. The essential differences are the use of ammonium phosphate instead of microcosmic salt, and the absence of the ammonium chloride held to be so necessary by Austin for the precipitation of either zinc or cadmium.

The next series of determinations (Nos. 9 to 12, Table II.) were made following exactly Dakin's conditions. The cadmium chloride solutions were diluted to a bulk of 150 c.c. and 0.5 c.c. of hydrochloric acid added, and then nearly neutralised with ammonia; then heated on a water bath and 35 c.c. (2.6 grms.) of ammonium phosphate solution added, and the heating continued for fifteen minutes. The phosphate solution was made exactly according to Dakin's directions and contained 80 per cent of $(\text{NH}_4)_2\text{HPO}_4$ to 20 per cent of $\text{NH}_4\text{H}_2\text{PO}_4$. After warming, the precipitates were allowed to stand over night before filtering; they were flocculent at first, became partly crystalline on warming, and after standing over night consisted entirely of large scale-like crystals of a pearly lustre, which settled immediately and were readily washed. They were filtered on asbestos in a Gooch crucible and washed first with a 1 per cent solution of the precipitant, then with 60 per cent alcohol, next dried and finally ignited, using a low flame at first, to pyrophosphate, and weighed.

As the asbestos used by Dakin was slightly soluble in the ammonium phosphate, he determined the weight of the Gooch crucible after weighing the precipitates—dissolving out the pyrophosphate with dilute nitric acid. The results in the table give both methods of procedure, direct weight and by difference. The determinations made by dissolving out the precipitate are invariably high, while those made by direct weight are slightly low. These figures lead to an investigation of the solubility of the asbestos in nitric acid as well as in the phosphate solution, which showed constant loss with either solution, even where the asbestos had been treated first with boiling nitric acid and then been allowed to stand one portion with nitric acid, the other with a strong ammonium phosphate solution for two weeks, and explained satisfactorily the error in using an asbestos filter.

To avoid this source of error a series of determinations was next made in which the precipitates were filtered on balance papers. This precipitate is particularly well adapted to this method, as the crystals are large, easily washed, and show no tendency to creep or run through. The reagent used was 100 per cent $(\text{NH}_4)_2\text{HPO}_4$, which we believe better than the mixture used by Dakin, as the dihydrogen ammonium salt gives no precipitate with cadmium. It is easily obtained by adding ammonia to the purchased reagent till it gives a slight pink with phenolphthalein.

The conditions for precipitation were as follows:—

To the cadmium chloride solution diluted to 150 c.c. and barely acid with hydrochloric acid add 35 c.c. (2.9 grms) of $(\text{NH}_4)_2\text{HPO}_4$ about fifteen times the weight of the cadmium present, and allow to stand over night. In Nos. 13–16 (see Table II.) the precipitant was added to the warm solution and then heated on a water-bath for fifteen minutes. This practice, while causing the conversion to the crystalline condition to take place more rapidly, is not to be recommended, as there is danger of the composition of the precipitate being changed by loss of ammonia. The precipitation is best made in the cold (Nos. 17–20), then allowed to stand over night.

TABLE I.

No.	Solution taken, c.c.	KCN, in grm.	Amperage.	Time, in hours.	Bulk, in c.c.	Cadmium in grm.
1.	30	I	0.15	16	160	0.2088
2.	30	I	0.15	16	160	0.2088
3.	30	I	0.15	16	160	0.2090
4.	30	I	0.1–0.15	16	160	0.2089
5.	30	I	0.1–0.15	16	160	0.2086
6.	30	I	0.1–0.15	16	160	0.2088

TABLE III.

No.	Cadmium taken, in grm.	Weight of precipitate dried at 100–103° C.	Cadmium calculated from $\text{CdNH}_4\text{PO}_4\text{H}_2\text{O}$.	Error, in terms of cadmium.
1.	0.2088	0.4427	0.2044	–0.0044
2.	0.2088	0.4382	0.2025	–0.0063
3.	0.2088	0.3965	0.1830	–0.0258
4.	0.2088	0.3715	0.1715	–0.0373
5.	0.2088	0.3430	0.1583	–0.0505
6.	0.2088	0.3429	0.1583	–0.0505
7.	0.2088	0.3306	0.1526	–0.0562
8.	0.2088	0.3346	0.1544	–0.0544

Remarks.

Nos. 1 and 2.—Heated one hour and filtered at once.
Nos. 3 and 4.—Heated on water-bath one hour.
Nos. 5 and 6.—Boiled gently one hour.
Nos. 7 and 8.—Boiled moderately.

TABLE IV.

	Theory for $\text{CdNH}_4\text{PO}_4\text{H}_2\text{O}$.	Crystalline precipitate.	Pulverulent precipitate.
	Per cent.	Per cent.	Per cent.
NH_3	7.00	6.75	0.48
H_2O	11.09	10.83	1.47
P_2O_5	22.16	29.40	24.31
CdO	52.75	52.83	73.56
	100.00	99.81	99.82

Precipitates 13–20 were all filtered on balance papers (after drying at 105° C. for several hours), washed first with a 1 per cent solution of $(\text{NH}_4)_2\text{HPO}_4$, then with 60 per cent alcohol, and weighed after drying to constant weight at 100–103° C.

In Nos. 15, 16, 18, and 20 the precipitates were dissolved in dilute nitric acid, evaporated and ignited in platinum to $\text{Cd}_2\text{P}_2\text{O}_7$. Weighing as $\text{CdNH}_4\text{PO}_4\text{H}_2\text{O}$ is to be preferred, as it is shorter and the danger of reduction and volatilisation is avoided. These results are shown in Table II.

The next series was made to determine the effect of ammonium chloride, as this salt is likely to be present in varying quantities. The conditions were identical with Nos. 17–20 in Table II., except that each solution contained 15 grms. of ammonium chloride. The results expressed in grms. of cadmium were 0.2080, 0.2082, 0.2081, 0.2083. The filtrates gave in each case a slight but distinct precipitate of cadmium sulphide when tested with hydrogen sulphide. These results show that ammonium chloride, in any such quantity, exerts a slight solvent action, and is to be avoided when great accuracy is required.

The effect of heating on the precipitate was next investigated, and the results given in Table III.

The danger, already mentioned, of hastening the conversion to the crystalline condition by heating is fully shown by Table III. In Nos. 1 and 2 the $\text{CdNH}_4\text{PO}_4\text{H}_2\text{O}$ precipitates were heated one hour in a water-bath, until they were entirely crystalline, and then filtered at once; the other conditions were the same as Nos. 13–20 in Table II., where accurate results were obtained. The physical properties of the precipitates were changed by the heating, the crystals were finer, and a portion of the pre-

precipitate was decidedly pulverulent. Nos. 3 and 4 were heated at a higher temperature on the water-bath until the precipitates became crystalline, and then stood over night before being filtered. In these, a larger proportion of the pulverulent precipitate was noticed. Nos. 5 and 6 were boiled gently; here the precipitates consisted chiefly of the dense pulverulent particles with a small quantity of coarse scale-like crystals resembling those formed in the cold. In Nos. 7 and 8 the boiling was more vigorous, and here the precipitates were entirely pulverulent, and in no way resembled those obtained in the cold.

This change in appearance, together with the low results, indicate certainly a change in the composition of the precipitate. Ammonia is given off in noticeable quantities during the boiling.

The coarse crystalline precipitate formed in the cold, and the fine pulverulent precipitate, made by boiling small quantities in separate beakers, on account of great trouble due to bumping, were analysed, with the results given in Table IV.

The analyses show the loss of both water and ammonia by boiling, and suggests that the normal cadmium orthophosphate would be produced were the boiling sufficiently prolonged, and at the same time confirm the determination of the water of crystallisation in the crystalline precipitate.

The points which we wish to emphasise are:—

1. That the electrolytic determination of cadmium is most accurate and satisfactory, provided a large excess of potassium cyanide and the presence of other salts are avoided.

2. That the carbonate method is the most troublesome, and the least accurate.

3. That cadmium ammonium phosphate contains one molecule of water of crystallisation, and can be dried without decomposition at $100-103^{\circ}\text{C}$.

4. That Austin's method for cadmium is unsatisfactory.

5. That asbestos filters should be avoided on account of the solvent action of either ammonium phosphate or nitric acid.

6. That cadmium can be determined with great accuracy by precipitating in the cold, in a neutral solution by a large excess of $(\text{NH}_4)_2\text{HPO}_4$, and allowing to stand over night; it can be weighed on balanced filters or ignited to pyrophosphate. If precipitated in a boiling solution or on prolonged boiling it is liable to change in composition and give low results.

We recommend this method as preferable to the carbonate method in all respects, and while no more accurate than the electrolytic, it has the practical advantage of requiring no extraordinary or expensive apparatus.

NOTICES OF BOOKS.

Engineering Chemistry. A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists, and Engineers. Second Edition. By THOMAS B. STILLMAN, M.Sc., Ph.D. With 132 Illustrations. Easton, Pa.: The Chemical Publishing Company, 1900. Pp. 503.

THIS valuable work is not intended for beginners, as may be gathered from the title. Students commencing quantitative work can perform (as the author tells us), with advantage, the first eleven exercises given in this work with proper supervision, and then select a course of study suitable to their advancement; either for iron and steel chemistry; railroad laboratory practice; the technical application of water supply; the chemical technology of fuels, &c.

These eleven exercises referred to comprise such typical examples as the determination of iron in iron-wire, of alumina in potash alum, of lead in galena, of iron in hematite, of phosphorus pentoxide in calcium phosphate, &c.

The articles upon gas analysis and valuation, blast-furnace practice, the heating value of fuels, the purification of water for technical purposes, lubrication, car illumination, and the examination of Portland cement, have all received special attention, since these topics, at the present time, form a considerable portion of the work and investigations of engineers; a number of articles on the above subjects have been contributed by experts in each line of study.

As is only too often the case in books of this class, the section devoted to water analysis is incomplete and old-fashioned. The untrustworthy and discredited method of estimating the organic matter in water by the "albumenoid ammonia" process is given in full, while no mention is made of that beautiful and exact method devised by the late Sir E. Frankland and Prof. Armstrong, known as the "combustion process." It is true that the latter method requires more expensive apparatus than does the former, but that should not be a drawback in a properly equipped laboratory; probably the reason why the combustion process is so often neglected lies in the fact that it requires much more intelligence and manipulative skill for its proper performance, but that *again* should be no drawback in a properly conducted laboratory.

The book is well arranged and printed, and its value as a whole is considerable; it should indeed be found in all commercial laboratories. It is provided with a very extensive table of contents and a large index.

Handbook of Practical Hygiene. By D. H. BERGEY, A.M., M.D., Easton, Pa.: The Chemical Publishing Company. Pp. 164.

THE object for which this book was prepared was to afford a help to students in the sanitary analysis of air, water, soil, and the principal food materials, and in testing the ventilation of buildings, &c. There are several excellent hand-books on these subjects in German, as well as a number of general treatises on hygiene in English, but there has been a lack of any short concise laboratory guide.

Here as a general rule only the more simple and ready methods now in use have been used. The subject of food analysis has been gone into far enough to permit the detection of the more common forms of adulteration that are likely to be met with.

The book is divided into five parts, viz.:—I. Atmospheric air; II. Water; III. Soil; IV. Sanitary Analysis of Foods, and V. Ventilation and Heating, and each part is again sub-divided into several chapters.

With regard to the chapters on water analysis we may point out that the old-fashioned, untrustworthy albumenoid ammonia method has been given undue prominence, while the best and most delicate method is entirely neglected. There are a good number of the most modern methods given for estimating nitrogen as nitrates and nitrites, but none of them compare with the old indigo method for speed and simplicity.

The book has been very carefully compiled, and will well repay perusal not only by the student but by the practical analytical chemist as well.

Die Chemische Organisation der Zelle. By Dr. F. HOFMEISTER. Braunschweig: Friedrich Viewig und Sohn.

IN this paper, which was written for the Hamburg Scientific Society, an attempt is made for the first time to elucidate the structure of protoplasm by investigating the chemical processes occurring in the cell. The author believes that a fuller knowledge of the chemistry of these processes and of the substances elaborated by them will do more towards solving the problem of the essential nature of living protoplasm than the most careful micro-

scopic work, though he by no means under-estimates the value of the latter method. Bearing in mind Dr. Hofmeister's distinguished researches on pepsin and the peptones, we have every reason for believing in his ability to throw light upon this more complex and extended question. Taking the liver cell as a typical example, he enumerates the various substances produced by it, such as bilirubin and cholic acid, the exact composition of which is yet to be determined, and dwells upon the theory of the probable existence in the cell of a ferment corresponding to each chemical process, and the recent discoveries of the power of the animal body to create antidotes, antitoxins, &c. Many of the ideas contained in the paper are original, and though written chiefly from a physiological point of view, the chemist will find in it much to interest him and to suggest profitable subjects for research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 23, December 2, 1901.

Induced Radio-activity provoked by Radium Salts.—P. Currie and A. Debiere.—It is known that all bodies become radio-active when they are enclosed in a vessel containing a solid salt of radiferous barium. This radio-activity said to be induced, can also be obtained by replacing the solid radium salt by an aqueous solution, and the effects produced are more regular by this latter method. The various solid bodies experimented with (copper, platinum, lead, tin, aluminium, glass, paper, wax, zinc sulphide, &c.), acquire the same activity when placed in contact with the exciting agent, under the same conditions. The radiating power of the bodies is, in the same manner as radium itself, composed of rays deviated or non-deviated by the magnetic field. The induced activity is independent of the pressure and the nature of the gas surrounding the exciting agent. Certain substances (those phosphorescent to light and others) become luminous when placed in contact with radium, zinc sulphide being especially brilliant under these conditions. Glass also acquires phosphorescent properties, especially Thuringen glass. The limit of activity produced with the same exciting agent depends only on the quantity of radium which is in solution.

Influence of Radio Active Substances on the Luminescence of Glass.—Alix de Hemptinne.—Some time ago the author discovered that a gas which becomes luminous when subjected to a certain pressure under the influence of electric vibrations becomes luminous at a higher pressure under the influence of X-rays. He now establishes the fact that if a tube containing rarefied gas, through which an electric current is passing, is brought near some of the radio-active materials, the gas becomes luminous at a pressure of 44 m.m., while away from the exciting agent it does not become luminous until a pressure of 33 m.m. is produced. Also the colour, which was a red-violet in the latter case, becomes yellowish green under the influence of radio-active substances.

Study of the Tin-Aluminium Alloys.—Léon Guillet.—Tin-aluminium alloys have been investigated by M. Gautier, but chiefly from the point of view of fusibility. So far, however, no compounds of tin and aluminium have been isolated. The curve of fusibility predicts the compound AlSn . The author was able to isolate the two compounds Al_4Sn and AlSn , in the crystalline state and also in the

state of a crystalline powder. All the experiments were made on 3 kilos. of material, but the volatilisation of the tin rendered the experiments difficult. Tin estimations were made electrolytically. These experiments lead to the conclusion that—(1) All the reactions are extremely violent, and there are enormous losses of tin in the form of stannic acid. (2) The limiting compound formed is Al_4Sn . (3) All experiments containing more tin than that corresponding to AlSn leave no metallic residue. (4) All the portions of alloy contain considerable quantities of free aluminium (6 per cent to 13 per cent). (5) The quantity of tin in the alloy does not increase regularly with the initial quantity employed.

Action of Pyridic Bases on Tetrahalogenated Quinones.—Henri Imbert.—The oxidation derivative of the body $\text{C}_5\text{H}_4\text{N}=\text{C}_6\text{Cl}_2\text{O}_2=\text{OH}$, the preparation of which has already been described by the author, and of which the percentage composition corresponds to the formula $\text{HO}-\text{C}_5\text{H}_2\text{N}=\text{C}_6\text{Cl}_2\text{O}_2$ shows that the formulæ is the correct one. An examination of two derivatives of the primitive body show the existence of three ketonic functions, of which two neighbours, in a trichlorotriketopentamethylenic radicle, analogous to that which Hantzsch obtained during the oxidation of chloro and bromanilic acids. The chlorohydrate of pyridyltrichlorotriacetopentamethylene gives the possibility of a choice between the two conceivable formulæ, to represent the derivatives proving the action of pyridic bases on tetrahalogenated quinones, $\text{C}_5\text{H}_4\text{N}=\text{C}_6\text{Cl}_2\text{O}_2=\text{OH}$ or $\text{HO}-\text{C}_5\text{H}_2\text{N}=\text{C}_6\text{Cl}_2\text{O}_2$, for only the first agrees with the formation of the preceding derivatives.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., No. 13.

Researches on the Oxides of Chlorine.—A. Reyckler.—Already inserted in full.

Peroxide of Chlorine as a Sterilising Agent for Potable Waters.—A. Reyckler.—To 5 litres of water, a calculated quantity of a freshly prepared solution of the peroxide was added, so as to form a solution containing 0.003 grm. of ClO_2 per litre, equal to 2.22 c.c. of decinormal thiosulphate. After thirty-five minutes the water was coloured distinctly blue by starch emulsion. The chlorometric value per litre was then 1.51 c.c. of thiosulphate. After two hours thirty minutes, the blue colour was less intense and the titration value was 1.5 c.c. of thiosulphate. After seven hours thirty minutes, there was a violet-rose colour and the titration required 1.41 c.c. of thiosulphate. After twenty-three hours, there was only a faint rose colour and only 1.37 c.c. of thiosulphate were required. The chlorometric value had therefore decreased to six-tenths of its original figure.

Aluminate of Magnesium.—Em. Dufau.—Already inserted in full.

Hydrogenation of the Incomplete Carbides in the presence of various finely-divided Metals.—P. Sabatier and J. B. Senderens.

Action of various finely-divided Metals on Ethylene and Acetylene.—P. Sabatier and J. B. Senderens.

Secondary Products formed in the Action of Sulphuric Acid on Wood-Charcoal.—A. Verneuil.

Myrcenol and its Constitution.—P. Barbier.—These four papers have been already noticed.

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 31, 1901.
THURSDAY, Jan. 2, 1902.
SATURDAY, " 4, "

Royal Institution, 3. (Christmas Lectures to Young People). "On Waves and Ripples in Water, Air, and Ether," by Professor J. A. Fleming, M.A., F.R.S., D.Sc.

INDEX.

ABERDEEN University, 120
 Aberystwyth, University College of Wales, 112
 Accumulator Industries, Limited, 51
 Acetone, action of hypophosphorous acid on, 83
 ethylic, action of fuming sulphuric acid on, 304
 propylic, action of fuming sulphuric acid on, 304
 Acetones, halogen compounds of, electrolytic preparation of, 304
 Acetylacetone, action of sulphuretted hydrogen on, 60
 Acetylene, reactions with cuprous chloride dissolved in neutral solution of potassium chloride, 24
 Acid, α -ethyltrichlorallylic, new synthesis of, 274
 anthranilic, malonic ether of, formation of indigo from, 243
 arsenic, acidimetry of, 47
 decane - dicarboxylic, normal, 263
 carbonic in water, estimation, 80, 92, 101, 145, 158, 164
 diethylamidobenzoylbenzoic, tetrachlorised and derivatives, 232
 dimethylamidobenzoylbenzoic, tetrachlorised and derivatives, 232
 dioxyisopropylhypophosphorous, 292
 dithionic, oxidation of sulphurous acid to by metallic oxides, 287
 gallic, derivatives, 299
 glycerophosphorous and glycerophosphites, 242
 homoallantoic and pyruvic, 231
 hydrobromic, action of silver on, 94
 hydrochloric, free, in gastric juice, 243
 hypophosphorous, action on acetone, 83
 isopyromucic, 72
 nitric, action on methyl dimethyl-aceto-acetate, 276
 nitrohydroxylamic, 292
 nitronaphthalic, esterification of, 263
 orthomono-chlorobenzoic, thermic data relative to, 12
 orthomonoiodobenzoic, thermic data relative to, 12
 parasulphanilic, acidimetric value, 36
 phosphoric, acidimetry by means of baryta-water, 269
 and chlorides of alkaline earths, 47

Acid reactions of two bases placed simultaneously in presence of, 35
 phosphorous, etherification by glycerin and glycol, 304
 pyromucic, 72
 pyruvic, action of urea on, 231
 urethane on, 219
 silicic, and tungstic acid, separation, 3
 sulphuric, action of fuming on ethylic and propylic aldehydes and acetones, 304
 and manganese dioxide, oxidation of benzinic carbides by, 242
 as a typhoid disinfectant, 161
 sulphurous, oxidation to dithionic acid by metallic oxides, 287
 trichloroacetic, reactions, 268
 trimethylsuccinic, bromination, 300
 tungstic, and silicic acid, separation, 3
 determination, 75
 separation from silica, 75
 undecylenic, hydrobromides of, 263
 Acids, action on amine salts, 36
 benzoylised, derivatives of, 32
 dialcylamidobenzylbenzoic, 32
 dialcylamido - ortho - benzoylbenzoic and derivatives, 12
 fatty, benzoylation in presence of ammonia, 274
 hydroxybutyric, optically active, 287
 in vegetables, formation, 208
 nitrating, relationship of cellulose to, 61
 of complex function, titration, 11
 organic, solubility of phosphatic manures in, 199
 pyrogallol sulphonic, 96
 tricarballylic, synthesis of allyl-substituted, 287
 Acidity in stem, leaf, and flower of a plant, distribution, 208
 Ackroyd, W., circulation of salt and its bearing on chemico-geological problems, 56
 distribution of chlorine in Yorkshire, 185
 inverse relation of chlorine to rainfall, 176
 Adams, J., and J. Knight, "The Self-educator in Chemistry" (review), 184
 Affinity, residual, part played by in formation of substitution derivatives, 301
 Air, Linde, generator gases produced by, 155
 Albumin, isatinic derivative, formation, 208

Alcohol, butylic, synthesis of normal, 97
 ethylic, action on barium ethylate, 97
 methylic, and iodide of methyl, molecular combination formed by, 231
 Alcohols, non-saturated, oxidation by action of contact, 292
 secondary and tertiary, action of contact on, 60
 "Alcool de l'Alambic et de l'Alcometrie, Historique de l'" (review), 241
 Aldehyde, benzoic, action on sodium menthol, 47
 ethylic, action of fuming sulphuric acid on, 304
 formic, importance as product of partial combustion of organic compounds, 15
 oxynaphthoic, union of camphor with, 47
 propylic, action of fuming sulphuric acid on, 304
 Aldehydes, acetylenic, synthesis, 60
 action of acid chlorides on in presence of zinc chloride, 36
 "Alkali, &c., Works, Thirty-seventh Annual Report" (review), 277
 Alkalis of complex function, titration, 11
 preparation, 108
 Alkaloids, vegetable, action on indicators, 60
 Alkyls, displacement from phenols by nitration, 23
 Allen, A. H., and J. M. Matthews, "Commercial Organic Analysis" (review), 184
 Alloys, aluminium-copper, 256
 aluminium-tin, 163, 316
 white-metal, analysis, 167
 Alumina, volumetric determination for technical purposes, 296, 306
 and ferric oxide, mutual action at incipient white heat, 305
 Aluminium, 249
 and molybdenum, alloys of, 96
 as an electrical conductor, 215
 bromide, action on acyclic chlorised hydrocarbons, 12
 chloride and alkaline chlorides, compounds, 304
 tin alloys, 163, 316
 American v. English spelling, 10
 Amides, formation, 274
 Amido-methylhydrindene, 22
 Amine derivatives of binaphthylene glycol, 242
 Amines, aromatic, action of sulphochloride of phosphorus, 48
 benzenoid, relations between physical constants and constitution in, 221

Amines, fatty, action of gaseous ammonia on chlorohydrate of, 84
 Aminoazo-compounds, influence of substitution on formation of, 297
 Ammonia, action on benzyl chloride, 242
 on metals at high temperatures, 264
 "Ammonia and Coal-tar" (review), 230
 estimation in its salts, 10, 35
 59
 free, 268
 from polluted sea-water, absorption by *Ulva latissima*, 176
 gaseous, action on chlorohydrates of fatty amines, 84
 Ammonium amalgam, 33, 291
 and other imidosulphites, 6
 chloride, decomposition of calcium-ammonium and lithium-ammonium by, 268
 dissolved in liquefied ammonia, electrolysis, 256
 metal, action on sulphuretted hydrogen, 279
 persulphate as substitute for lead peroxide in colorimetric estimation of manganese, 239
 "Analysis, Commercial Organic" (review), 184
 "Analysis, Elementary Organic" (review), 277
 volumetric, history of, 207
 Anderson, W. C., and G. Lean, aluminium-tin alloys, 163
 André, G., and M. Berthelot, formation of acids in vegetables, 208
 Angeli, A., and F. Angelico, nitrohydroxylamic acid, 292
 Angelico, F., and A. Angeli, nitrohydroxylamic acid, 292
 Anhydrite, hydration, 289
 Anhydrazetonebenzil, homo-
 logues of, 19
 Aniline, preparation, 108
 Antimony, double halides of, 194
 in presence of arsenic, determination, 256
 Apparatus, fat-extraction, 47
 Arabite, nitrated derivatives, 242
 Armstrong, E. F., equilibrium law as applied to salt separation and to formation of oceanic salt deposits, 177
 Dr., Frankland Memorial Lecture, 265
 H. E., and E. Horton, part played by residual affinity in formation of substitution derivatives, orienting influence of sulphur, 301
 and T. M. Lowry, bromo-camphor, 300

- Armstrong, H. E., derivatives of bromocamphor, 288
stereoisomeric and sulphonic derivatives of camphor, 22
Arndt, K., and G. von Knorre, oxidation of hydroxylamine, 220
Arsenic, determination of anti-mony in presence of, 256
in beer and articles of food, 173
Asarum canadense, essential oil of, constituents of, 286
Asbestos, 275
Assays, blowpipe, gold and silver buttons in, 181, 192
Astruc, A., action of vegetable alkaloids on indicators, 60
distribution of acidity in stem, leaf, and flower of a plant, 208
and J. Tarbouriech, acidimetry of arsenic acid, 47
Asymmetry of Zeeman effect, 218
"Atmosphere, Earth's, Researches on the Past and Present History of the" (review), 277
Atomic weights, 2
Auger, V., manganic phosphates, 60
Autenrieth, W., and P. Rudolph, action of sulphochloride of phosphorus on aromatic amines, 48
Azophenols, toluene, action of bromine on three, 19
- "BACTERIOLOGY, Determinative, a Manual of"** (review), 241
Balachowsky, D., separation of cobalt and nickel by electrolytic method, 24
Baly, E. C. C., and H. W. Syers, spectrum of cyanogen, 10
Bangor, University College of North Wales, 113
Barium preparation, 304
Bernadov, J. B., "Smokeless Powder, Nitrocellulose, and Theory of the Cellulose Molecule" (review), 218
Barton, E. H., and S. C. Laws, air pressures used in playing brass instruments, 302
Bases, action on amine salts, 36
pyridic, action on tetrahalogen quinones, 242, 316
reactions of two placed simultaneously in presence of phosphoric acid, 35
Baskerville, C., new element associated with thorium, 179, 187
Battersea Polytechnic, 123
Baud, E., compounds of aluminium chloride with alkaline chlorides, 304
Beadle, C., systematic chemical treatment of rags for paper-making, 257
Beam, W., and H. Leffmann, "Select Methods in Food Analysis" (review), 218
Bebbie, J., and G. Lunge, contributions to science of nitrocellulose, 30, 41, 55, 66, 76, 90, 100, 133, 144, 153, 166, 178, 189, 200
Bequerel, H., chemical effects produced by rays emitted by radium, 268
experiments with uranium, 83
Beer, detection and estimation of arsenic in, 173
Beilby, G. T., minute structure of metals, 163
and G. G. Henderson, action of ammonia on metals at high temperatures, 264
Belfast, Queen's College, 121
Bell, C. A., calibrating mercury pipette, 21
Benedict, F. G., "Chemical Lecture Experiments" (review), 160
"Elementary Organic Analysis, the Determination of Carbon and Hydrogen" (review), 277
Beneker, J. C., and J. W. Ellms, estimation of carbonic acid in water, 80, 92, 101, 145, 158, 164
Benzil, condensation with dibenzyl ketone, 264
Benzoquinones, tetrahalogen, action of pyridic bases on, 72, 84
Benzoyl chloride, action on trioxymethylene, 147
Benzyl, displacement by methyl in substituted nitrogen compounds, 276
Benzylamine, formation, 242
Benzylcamphor derivatives, 59
Benzyl chloride, action of ammonia on, 242
Benzylidene camphor derivatives, 59
Bergey, D. H., "Handbook of Practical Hygiene" (review), 315
Berthelot, M., acetylo-metallic radicles, 35
action of hydrogen peroxide on silver chloride, 231
chemical equilibrium, 24, 35, 47
reactions due to radium, 256
heat evolved during reaction between free oxygen and potassium pyrogallate, 256
neutralisation, titration of acids and alkalis of complex function, 11
and G. André, formation of acids in vegetables, 208
Bertrand, G., and L. Maquenne, active erythrites, 11
racemic erythrite, 36
Beryllium, new volatile salt of, 304
Besson, A., preparation of phosphorus oxide, 36
Bevan, E. J., and C. F. Cross, "Researches on Cellulose, 1895-1900" (review), 229
and R. L. Jenks, mixed esters of cellulose, and relationship of cellulose to nitrating acids, 61
Bibliography of steel works analysis, 249
Bidet, F., action of gaseous ammonia on chlorohydrates of fatty amines, 84
Binaphthylene glycol, amine derivative of, 242
hydrobromic and hydrochloric ethers of, 84
Birkbeck Institution, 108, 123
Birmingham University, 114
Bismuth, salicylate of, new crystallised, 310
Blackburn Municipal Technical School, 124
Blackler, M. B., estimation of ammonia in its salts, 35
Blake, R. F., and Prof. Letts, chemical and biological changes during treatment of sewage by bacteria beds, 161
Blanc, M., and A. Seyewetz, colourless compound of sodium tetrazotylsulphite with ethylnaphthylamine, and its transformation into a colouring-matter, 47
Bleaching textiles, electrolysis in, 156
"Blowpipe Analysis" (review), 267
assays, gold and silver buttons in, 181, 192
tests, 13
Bluman, N. J., monazite from New Granada, 175
Boilers, steam, chemistry of deposits in, 191
Bone, W. A., and D. S. Jerdan, decomposition of hydrocarbons at high temperatures, 7
union of carbon and hydrogen, 6
and C. H. G. Sprankling, bromination of trimethylsuccinic acid and interaction of ethylbromotrimethylsuccinate and ethylsodiocyanacetate, 300
synthesis of alkyl-substituted tricarballic acids, 287
Bongert, A., action of certain acid chlorides on methyl and ethyl sodacetylacetate, 292
decompositions of methylbutyryl-acetylacetate, 72
and L. Bouveault, nitration of acetylacetic ethers and their acide derivatives, 36
nitration product of acetylacetic ether, 60
Booth, E., needed reform in chemical nomenclature, 278
Borough Polytechnic Institute, 123
Botany, chemical names in, 183
Bouveault, L., and A. Bongert, nitration of acetylacetic ethers and their acide derivatives, 36
nitration product of acetylacetic ether, 60
Boyd, D. R., action of chlorides of phosphorus on aromatic ethers of glycerin, 264
Bradford Municipal Technical College, 115
Brass instruments, air-pressures used in playing, 302
Brauner, B., existence of a new element associated with thorium, 219
place of hydrogen in periodic system, 233
Brearley, H., bibliography of steel works analysis, 249
estimation of carbon in metals, 23, 59
and F. Ibbotson, analysis of white-metal alloys, 167
volumetric estimation of manganese, 247, 302
Brenans, P., iodine-phenyl ethereal derivatives, 72
Bristol, Merchant Venturers' Technical College, 114
University College, 113
British Association, 147
Address of the President, 125
to Chemical Section, 137
Brixton School of Chemistry and Pharmacy, 123
Bromacetophenone, action on sodium acetylacetone, 47
Bromine, action on three toluene azophenols, 19
Bromocamphor, 300
derivatives, 288
Brown, J. W., P. R. French, and S. P. Mulliken, importance of formic aldehyde as product of partial combustion of organic compounds, 15
Brown, O. W., and L. M. Dennis, potassium perselenate, 2
Browning, K. C., phosphorus suboxide, 300
Brunck, O., quantitative estimation of ozone, 232
Buchan, A., estimation of ammonia in its salts, 59
Buchanan, J., model which imitates behaviour of dielectrics, 240
Burgess, C. H., and D. L. Chapman, non-existence of suboxide of phosphorus, 264
H. E., two new substances in lemon oil, 9
Burrows, H., and W. A. Tilden, constitution of limettin, 283
Byrom, T. H., manganese in waters, 183
- CADMIUM** determination, 312
ferrocyanide, 170
Cæsium, 96
material, purification, 169
Calcium-ammonium, decomposition by ammonium chloride, 268
Calculations, chemical, abridgments in, 201
"Calico-printing and Dyeing, a Dictionary of Dyeing, Mordants, and other Compounds used in" (review), 255
Cambridge University, 110
Camphane series, 8
Camphor, stereoisomeric and sulphonic derivatives of, 22
union with oxy-naphthoic aldehyde, 47
Carbazoles, formation, 20
Carbides, benzinic, oxidation by manganese dioxide and sulphuric acid, 242
"Carbon and Hydrogen, the Determination of" (review), 277
union, 6
dioxide, decomposition, 8
nascent, as a chemical reagent, 164
estimation in metals, 23, 46, 59
Carbonates, determining small quantities, 299
Carbonic-oxide-hæmoglobin, behaviour in magnetic field, 85
Cardiff, University College of South Wales and Monmouthshire, 113
Carpenter, H. C. H., oxidation of sulphurous acid to dithionous acid by metallic oxides, 287
Carpenters' Company Technical Institute, 124
Carrara, G., and G. B. Vespignani, energy of some metallic hydrates deduced from hydrolysis of the salts, 280
Carre, P., etherification of phosphorous acid by glycerin and glycol, 304
Cash, J. T., and W. R. Dunstan, pharmacology of pseudoconitine and japaconitine, 27
pyraconitine and methylbenzaconitine, 38
Cassie, W., measurement of Young's modulus, 267
multiple transmission fixed-arm spectroscopes, 266
Castendyck, C., and C. Friedheim, silico-vanadio-molybdates, 295
Catalysis in concentrated solutions, 205, 213
Cavalieri, J., acidimetry of phosphoric acid by means of baryta water, 269
Cayvan, L. L., and A. G. Woodman, determination of phosphates in potable waters, 69, 78
Cellulose fermentation, 220
mixed esters of, 61
relationship to nitrating acids, 61
sugars from, 7
"Cellulose Molecule, Theory of, Smokeless Powder, Nitrocellulose, and" (review), 218
"Cellulose, Researches on, 1895-1900" (review), 229
Cerite, 136
Chabrie, C., cæsium, 96
Chalcopyrite, 29
Chapman, D. L., and C. H. Burgess, non-existence of suboxide of phosphorus, 264
Chappuis, P., gas thermometry, 267
Charabot, E., and A. Hébert, mechanism of etherification in plants, 147
Charon, E., and D. Zamanos, constitution of piccol, 268
Chassy, A., formation of ozone, 279
Chavanne, M., pyromucic and isopyromucic acids, 72
Chavastelon, R., reactions of acetylene with cuprous chloride dissolved in neutral solution of potassium chloride, 24
Chelsea, South-Western Polytechnic, 123
"Chemical Analysis, Qualitative, Organic and Inorganic" (review), 276
"Chemical Essays of Charles William Scheele" (review), 255
"Chemical Philosophy, Introduction to the Study of" (review), 278

- "Chemical Lecture Experiments" (review), 160
- "Chemical Society, Memorial Lectures delivered before, 1893-1900" (review), 241
- calculations, abridgments in, 201
- combination, theory, 9
- education, 151
- laboratory at Wiesbaden, 108
- lectures, 122
- literature, system of indexing, 203, 210
- names in botany, 183
- nomenclature, needed reform in, 278
- reactions due to radium, 256
- limit, and that of product PV in gases, 242
- Society, 6, 19, 259, 263, 273, 278, 286, 291, 297, 303
- library catalogue, 301
- "Chemistry, Elementary Experimental Inorganic" (review), 229
- "Chemistry, Elementary Principles of" (review), 302
- "Chemistry, Engineering" (review), 315
- "Chemistry, Inorganic, a Short Manual of" (review), 218
- "Chemistry, Inorganic, Guide to the Study of" (review), 291
- "Chemistry, Inorganic, Laboratory Companion for Use with Shennstone's" (review), 231
- "Chemistry of Paints and Painting" (review), 277
- "Chemistry, Organic, Practical, for Advanced Students" (review), 230
- "Chemistry, the Self-educator in" (review), 184
- British, position at dawn of twentieth century, 137
- mechanical, verification of a law of, 11
- Chester, F. D., "Manual of Determinative Bacteriology" (review), 241
- Chlorides, acid, action on aldehydes in presence of zinc chloride, 36
- on methanol, 60
- on methyl and ethyl sodiacetylacetates, 292
- alkaline, and aluminium chloride, compounds, 304
- Chlorine and gold compounds, 291
- in Yorkshire, distribution, 185
- inverse relation to rainfall, 176
- oxides of, 234
- peroxide as a sterilising agent for potable waters, 316
- test for, 13
- Chlorobromides, thallium, 24
- Chlorodibromobenzenes, 265
- Church, A. H., "The Chemistry of Paints and Painting" (review), 277
- Cirencester, Royal Agricultural College, 115
- City and Guilds of London Institute, 122
- of London College, 123
- Clarke, F. W., alkaline reactions of some natural silicates, 312
- G., and F. S. Kipping, amidomethylhydriene, 22
- Clayton, E. G., asbestos, 275
- incrustation from Stone Gallery of St. Paul's Cathedral, 275
- Clermont, A., reactions of trichloroacetic acid, 268
- "Coal-tar and Ammonia" (review), 230
- industry in England and Germany, relative progress during past fifteen years, 185, 197
- Cobalt and nickel, separation by electrolytic method, 24
- Cohen, J. B., "Practical Organic Chemistry for Advanced Students" (review), 230
- and H. D. Dakin, reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide, 287
- Cohn, R., and A. Rosenheim, double metallic thiocyanates, 243
- Coil, equivalent radius of, 301
- Coils, circular, circular filaments or circular magnetic shells equivalent to, 301
- College, South African, 71
- Colleges, 109
- Collie, J. N., decomposition of carbon dioxide, 8
- Colouring-matters, new, 12
- "Colours, Oils, and Varnishes, Painters'" (review), 277
- Colson, A., action of bases and acids on amine salts, 36
- inversion-points of dilution, 231
- Conductor, electrical, aluminium as, 215
- Contact, action on secondary and tertiary alcohols, 60
- Copper-aluminium alloys, 256
- estimation in biological researches, 220
- sulphate and sodium sulphate, solubility of mixtures of, 96
- crystallisation, 42
- variation with temperature of thermo-electromotive force, and of electric resistance of, 217
- Cork, Queen's College, 122
- Corstorphine, R. H., and G. G. Henderson, condensation of benzil with dibenzyl ketone, 264
- Crafts, J. M., catalysis in concentrated solutions, 205, 213
- Crookes, Sir W., and J. Dewar, London water supply, 30, 94, 144, 190, 251, 311
- Cross, C. F., and E. J. Bevan, "Researches on Cellulose, 1895-1900" (review), 229
- and R. L. Jenks, mixed esters of cellulose, and relationship of cellulose to nitrating acids, 61
- Crossley, A. W., preparation and properties of 2:6-diketo-4-isopropylhexamethylene, 9
- and H. R. Le Sueur, substituted dihydrobenzenes, 300
- Curie, P., and A. Debierne, radio-activity of radium salts, 25, 83, 316
- Cushman, A., flame colouration of nickel, 291
- Cyanide, estimation in presence of a chloride, 197
- Cyanides in gas-works, extraction, 223
- Cyanogen, spectrum of, 10
- Cymene, halogen derivatives from substituted nitro-camphanes, 8
- DAKIN, H. D., and J. B. Cohen, reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide, 287
- Dawson, H. M., and J. McCrae, metal-ammonia compounds in aqueous solution, 21
- De Forcrand, M., calculation of heat of volatilisation and heat of fusion of certain elements, 208
- minimum value of total heat of combination, Q, 256
- molecular weight of chloral hydrate at temperature of ebullition, 184
- thermic examination of hydrate of solid soda, 84
- thermometric examination of solid potassium hydrates, 72
- value of molecular weights at temperature of ebullition, 146
- De Hemptinne, A., influence of radio-active substances on the luminescence of glass, 316
- D'Hommée, R., action of ammonia on benzyl chloride, and conditions of formation of benzylamine, 242
- De Koninck, L. L., history of volumetric analysis, 207
- Deacon, E. R., tintometer in water analysis, 59
- Debierne, A., and P. Curie, radio-activity of radium salts, 25, 83, 316
- Defournel, H., action of saccharine on urea from phenylhydrazine, 232
- basic saccharinate of quinine, 232
- Delacré, M., researches on isomerisations of pinacone and derivatives, 263
- Delage, M., pyrogallol sulphonic acids, 96
- Delange, K., and C. Moureu, synthesis of acetylenic aldehydes, 60
- Délepine, M., action of fuming sulphuric acid on ethylic and propylic aldehydes and acetone, 304
- imidodithiocarbonic ethers, 11
- Demaray, E., europium, 1
- Deniges, G., qualitative and quantitative determination of traces of antimony in presence of large proportion of arsenic, 256
- Dennis, L. M., and O. W. Brown, potassium perselenate, 2
- Descude, M., action of acid chlorides on aldehydes in presence of zinc chloride, 36
- action of benzoyl chloride on trioxymethylene in presence of zinc chloride, 147
- Dewar, J., nadir of temperature and allied problems, 49
- solid hydrogen, 281, 293
- and Sir W. Crookes, London water supply, 30, 94, 144, 190, 251, 311
- and G. D. Liveing, separation of least volatile gases of atmospheric air, and their spectra, 37, 51
- Dhéré, C., estimation of copper in biological researches, 220
- Dialdehyde, malonic, bromated, 219
- Diastase and yeast, combined action on starch granules, 21
- Diazo, inspiration from the immortals, 59
- Diazoamines, influence of substitution on formation, 297
- Dibenzoyldiphenylbutadiene, reduction, 19
- Dibenzoylpropane, reduction of, 19
- Dichlorobromo-benzenes, 265
- Dichloro-orthoxylenes, 72
- "Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing" (review), 255
- Dielectrics, model which imitates the behaviour of, 240
- Dihydrobenzenes, substituted, 300
- Diketo-isopropylhexamethylene, preparation and properties, 9
- Dilution, in version-points, 231
- Dinaphthoxanthene, 60
- Dinitro-orthoanisidine, 263
- Diphenylenephensylmethane, coloured derivative of, synthesis of, 35
- Disinfectant, typhoid, sulphuric acid as, 161
- "Distillation, Recherches Retrospectives sur l'Art de la" (review), 241
- Divers, E., and T. Haga, nitrilosulphates, 7
- and M. Ogawa, ammonium and other imidosulphites, 6
- Doctors of Medicine and Naturalists, Russian, Congress, 210
- Dublin, Royal College of Science, 122
- University, 110
- Dufau, E., aluminate of magnesium, 222
- Duffy, L., volumetric estimation of manganese, 248
- Dujardin, J., "Recherches Retrospectives sur l'Art de la Distillation, Historique de l'Alcool de l'Alambic et de l'Alcometrie" (review), 241
- Dundee, University College, 119
- Dunstan, W. R., and J. T. Cash, pharmacology of pseudoconitine and japaconitine, 27
- of pyraconitine and methylbenzaconine, 38
- and T. A. Henry, nature and origin of poison of Lotus arabicus, 26
- Dupré, A., and H. W. Hake, "A Short Manual of Inorganic Chemistry" (review), 218
- Durham College of Science, 117
- "Dyeing and Calico Printing, a Dictionary of Dyes, Mordants, and other Compounds used in" (review), 255
- "Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing, a Dictionary of" (review), 255
- EARTHS, alkaline, chlorides of, and phosphoric acid, 47
- "Earth's Atmosphere, Researches on the Past and Present History of the" (review), 277
- East London Technical College, 124
- Edinburgh, Heriot-Watt College, 121
- University, 120
- Education, chemical, 151
- "Electrical Engineering Formulae, Pocket-book of" (review), 47
- resistance, effect of a high frequency oscillatory field on, 10
- Electrolysis in bleaching textiles, 156
- Element, new, associated with thorium, 179, 187, 219
- Elements, calculation of heat of volatilisation and heat of fusion of, 208
- Ellms, J. W., and J. C. Beneker, estimation of carbonic acid in water, 80, 92, 101, 145, 158, 164
- Elschner, C., utilisation of fluorine gases formed in manufacture of superphosphates, 222
- "Engineering Chemistry" (review), 315
- English v. American spelling, 10
- Epibromhydrine, action on sodium benzoyl acetic ethers, 24
- Epichlorhydrine, action on sodium benzoyl acetic ethers, 24
- Equilibrium, chemical, 24, 35, 47
- law as applied to salt separation, and formation of oceanic salt deposits, 177
- Erythrite, racemic, 36
- Erythrites, active, 11
- Esters of acetylene series, condensation of phenols with, 263
- Ether, acetylacetic, nitration product of, 60
- malonic, of anthranilic acid, formation of indigo from, 243
- Ethers, acetylacetic, and their acidyle derivatives, nitration, 36
- aromatic, of glycerin, action of chlorides of phosphorus on, 264
- hydrobromic and hydrochloric, of binaphthylene-glycol, 84
- imidodithiocarbonic, 11
- nitric, constitution, 242
- reducing properties, 219
- sodium benzoyl acetic, action of epichlorhydrine and epibromhydrine on, 24
- Ethyl bromotrimethylsuccinate and ethylsodiocyanacetate, interaction, 300

- Ethyl naphthylamine, colourless compound of sodium tetrazotolyl sulphate with, 47
 sec-octyl tartrate and its dibenzoyl and diacetyl derivatives, 263
 sodacetylacetates, action of acid chlorides on, 292
 sodiocyanacetate and ethyl bromotrimethylsuccinate, interaction, 300
 Ethylate, barium, action of ethylic alcohol on, 97
 Europium, 1
 "Evolution, chemical, the Periodic Classification and the Problem of" (review), 196
 Examinations, Society of Arts, 153
 "Explosives, Annual Report of Her Majesty's Inspectors of" (review), 290
 Eyre, J. V., and R. Meldola, dinitro-orthoanisidine, 263
- F**
 FARMER, R. C., and P. F. Frankland, liquid nitrogen peroxide as a solvent, 275
 Fat-extraction apparatus, 47
 Fenton, H. J. H., sugars from cellulose, 7
 Ferrand, L., dichlor-orthoxylenes, 72
 Fertilisers, rate of nitrification of, 45, 57
 Filaments, circular, equivalent to circular coils, 301
 Fiquet, E., synthesis and properties of nitrile phenols, 232
 Fisher, H., and E. H. Miller, lead and cadmium ferrocyanides, 170
 Flame colouration of nickel, 291
 Fletcher, L., meteoric stones which fell near Zomba, British Central Africa, on Jan. 25, 1899, 4, 16, 34, 44, 65, 81, 91, 103
 Flower of a plant, distribution of acidity in, 208
 Fluorides, caesium-antimonious, 194
 "Food Analysis, Select Methods in" (review), 218
 "Food, the Cost of" (review), 241
 detection and estimation of arsenic in, 173
 "Formulæ, Electrical Engineering, Pocket-book of" (review), 47
 Forster, M. O., bromocamphor, 300
 camphane series, 8
 and W. Robertson, halogen derivatives of *p*-cymene from substituted nitrocamphanes, 8
 Fosse, R., amine-derivative of supposed bi-naphthylene glycol, 242
 di-naphthoxanthene, 60
 hydrobromic and hydrochloric ethers of bi-naphthylene glycol, 84
 transformation of two xanthodols into xanthenes by a new reaction, 304
 Fournier, H., oxidation of benzinic carbides by manganese dioxide and sulphuric acid, 242
 Frankland Memorial Lecture, 265
 Frankland, P. F., Address to Chemical Section of British Association, 137
 and R. C. Farmer, liquid nitrogen peroxide as a solvent, 275
 Fraps, G. S., and W. A. Withers, rate of nitrification of fertilisers, 45, 57
 French, P. R., S. P. Mulliken, and J. W. Brown, importance of formic aldehyde as product of partial combustion of organic compounds, 15
- Frappie, F. R., and T. W. Richards, solubility of manganous sulphate, 156
 Friedheim, C., and C. Castendyck, silico-vanadio-nolybdates, 295
 Fusion of elements, calculation of heat of, 208
- G**
 GALWAY, Queen's College, 122
 Gamgee, A., behaviour of oxy-hæmoglobin, carbonic-oxide-hæmoglobin, methæmoglobin, and derivatives, in magnetic field, 85
 Gardner, W. M., W. F. Laycock, and C. Rawson, "Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing" (review), 255
 "Gas Engineers' Pocket-book" (review), 242
 oxygen, action on cobalticyanide of potassium, and on chromous salts, 243
 thermometry, 267
 works, extraction of cyanides in, 223
 Gases, fluorine, formed in the manufacture of superphosphates, utilisation, 222
 generator, produced by means of Linde air, 155
 least volatile of atmospheric air, separation and spectra, 37, 51
 limit of chemical reactions and that of product PV in, 242
 liquefied in sealed tubes, method of manipulation, 279
 Gatehouse, F. B., estimation of cyanide in presence of a chloride, 197
 Gerin, F., and L. Vignon, nitrated derivatives of arabite and rhamnite, constitution of nitric ethers, 242
 nitric derivatives of pentacrythrite, 231
 nitromannite and nitrocellulose, 202
 reducing properties of nitric ethers, 219
 Glasgow and West of Scotland Technical College, 121
 Glass, luminescence of, influence of radio-active substances on, 316
 Glycerin, aromatic ethers of, action of chlorides of phosphorus on, 264
 Glycerophosphites and glycerophosphorous acid, 242
 Gnezda, J., formation of isatinic derivative of albumin, 208
 "Gold, Prospecting for" (review), 290
 and chlorine compounds, 291
 silver buttons in blowpipe assays, 181, 192
 ores, assaying of complex, 62, 74, 89, 98, 134
 Goldsmiths' Institute, 123
 Gomberg, M., triphenylchloromethane, 14
 Gray, J. M., numerical value of characteristic of water, 240
 Green, A. H., relative progress of coal-tar industry in England and Germany during past fifteen years, 185, 197
 Grimaux, A., and L. Lefevre, new colouring matters, 12
 Guerbet, M., action of ethylic alcohol on barium ethylate, 97
 Guillet, L., alloys of aluminium and molybdenum, 96
 copper-aluminium alloys, 256
 tin-aluminium alloys, 316
 Guntz, M., preparation of barium, 304
 Guyot, A., and A. Haller, dialcylamidobenzylbenzoic acids, 32
- Guyot, A., and A. Haller, dialcylamido-ortho-benzylbenzoic acids and derivatives, 12
 synthesis of coloured derivative of diphenylenephnylmethane, 35
 Gyzander, C. R., volumetric determination of alumina for technical purposes, 296, 306
- H**
 HÆMOGLOBIN compounds, electrolysis of, 85
 Haga, T., and E. Divers, nitrilosulphates, 7
 Hake, H. W., and A. Dupré, "A Short Manual of Inorganic Chemistry" (review), 218
 Hall, A. D., and F. J. Plymen, determination of available plant food in soils by use of dilute solvents, 298
 and E. J. Russell, determining small quantities of carbonates, 299
 Haller, A., new syntheses by molecules containing methylene group associated with negative radicals, 24
 and A. Guyot, dialcylamido-benzylbenzoic acids, 32
 dialcylamido-ortho-benzylbenzoic acids and derivatives, 12
 synthesis of coloured derivative of diphenylenephnylmethane, 35
 and J. Minguin, derivatives of benzylcamphor and of benzylidene-camphor, 59
 and H. Umbgrove, tetrachlorised dimethyl and diethylamidobenzylbenzoic acids and derivatives, 232
 Hantzsch, A., iodide of nitrogen, 244
 Harden, A., and S. Rowland, autofermentation and liquefaction of pressed yeast, 264
 Harrison, E. P., variation with temperature of thermoelectromotive force and of electric resistance of nickel, iron, and copper, 217
 Hawthorne, J., and Prof. Letts, absorption of ammonia from polluted sea-water by Ulva latissima, 176
 Heat evolved during reaction between free oxygen and potassium pyrogallate, 256
 of combination, Q, minimum value of total, 256
 of volatilisation and heat of fusion of elements, calculation of, 208
 Hébert, A., and E. Charabot, mechanism of etherification in plants, 147
 Helbronner, A., union of camphor with oxynaphthoic aldehyde, 47
 Henderson, G. G., and G. T. Beilby, action of ammonia on metals at high temperatures, 264
 and R. H. Corstorphine, condensation of benzil with dibenzyl ketone, 264
 Henry, L., action of acid chlorides on methanal, 60
 T. A., constituents of sandarac resins, 263
 and W. R. Dunstan, nature and origin of poison of Lotus arabicus, 26
 Heriot-Watt College, Edinburgh, 121
 Herting, O., McKenna's method of analysis of tungsten and chrome steels, 75
 Herzog, J., and W. Manchot, action of oxygen gas on cobalticyanide of potassium and on chromous salts, 243
 Hewitt, J. T., and J. N. Tervet, action of bromine on three toluene azophenols, 19
- Hill, A. C., taka-diastase, 23
 E. H., system of indexing chemical literature, adopted by U.S. Patent Office, 203, 210
 Hillebrand, W. F., warning against use of fluoriferous hydrogen peroxide in estimating titanium, 311
 Hinks, A. R., possibility of systematic error in photographs of moving objects, 163
 Hird, J. M., and F. G. Pope, derivatives of nitrotolyl-hydrazine, 263
 Hodgkinson, W. R., and L. Limpach, relations between physical constants and constitution in benzenoid amines, 221
 Hofmeister, F., "Die Chemische Organisation der Zelle" (review), 315
 Holmes, J., and T. E. Thorpe, paraffins in leaf of tobacco, 9
 Holroyd, G. W. F., electrolytic reduction of nitreurea, 274
 Hopkins, A. J., crystallisation of copper sulphate, 42
 Horn, D. W., and H. N. Morse, preparation of osmotic membranes by electrolysis, 104
 Horton, E., and H. E. Armstrong, part played by residual affinity in formation of substitution derivatives, orienting influence of sulphur, 301
 Howe, J. L., American V. English spelling, 10
 manganese in water, 278
 Humus and irreducible residue in bacterial treatment of sewage, 149
 Hurst, G. H., "Painters' Colours, Oils, and Varnishes" (review), 277
 Hurlley, W. H., chlorodibromo- and dichlorobromobenzenes, 265
 Hydrate, chloral, molecular weight at temperature of ebullition, 184
 cupric, action on solutions of metallic salts, 96
 estimation in presence of alkali carbonate, 202
 metallic, action on solutions of salts of other metals, 11
 Hydrates, metallic, energy of some, deduced from hydrolysis of the salts, 280
 potassium, thermometric examination of solid, 72
 Hydration, reactions of, 292
 Hydrocarbides, acyclic chlorised, action of bromide of aluminium on, 12
 Hydrocarbons, decomposition at high temperatures, 7
 "Hydrogen and Carbon, the Determination of" (review), 277
 union, 6
 in periodic system, 154, 233
 oxide higher than the dioxide, supposed formation, 273
 peroxide, action on silver chloride, 231
 fluoriferous, in estimating titanium, warning against, 311
 solid, 281, 293
 sulphide, reduction of trinitrobenzene and trinitrotoluene with, 287
 sulphuretted, action of ammoniacal metal on, 279
 on acetylacetone, 60
 Hydroxylonic derivatives, 242
 Hydroxylamine, oxidation, 220
 "Hygiene, Practical, Handbook of" (review), 315
 Hygrometric method, new, 302
- I**
 IBBOTSON, F., and H. Brearley, analysis of white-metal alloys, 167
 volumetric estimation of manganese, 247, 302
 Idria, T. H. W., "Notes on Essential Oils" (review), 255

- Imbert, H., action of pyridic bases on tetrahalogen benzoquinones, 72, 84
on tetrahalogen quinones, 242
on tetrahalogenated quinones, 316
- Imidosulphites, 6
- Immortals, inspiration from, 59
- Imperial College of Chemistry and Pharmacy, 124
- Incrustation from Stone Gallery of St. Paul's Cathedral, 275
- Index, subject-matter, of mining and metallurgy, 292
- Indexing chemical literature, 203, 210
- Indican, contribution to our knowledge of, 280
- Indicator for determining total acidity of wines, 64
- Indicators, action of vegetable alkaloids on, 60
- Indigo, formation from malonic ether of anthranilic acid, 243
- Ink, sympathetic, 72
- Inspiration from the immortals, 59
- Institute of Chemistry, 12, 84, 289
- International association for testing materials, 147
- Iodine-phenyl ethereal derivatives, 72
- Ions, colour of, 146
nomenclature of, 162, 279
- Iridium in platinum ores, 216
- Iron-mould spots, 136
- Iron separation, 256
variation with temperature of thermo-electromotive force and of electric resistance of, 217
- JAPACONITINE**, pharmacology of, 27
- Japp, F. R., and W. Maitland, formation of carbazoles, 20
and A. N. Meldrum, homologues of anhydrazetone-benzil, 19
- and A. C. Michie, reduction of dibenzoylpropane and dibenzoyldiphenylbutadiene, 19
- Jenks, R. L., C. F. Cross, and E. J. Bevan, mixed esters of cellulose and relationship of cellulose to nitrating acids, 61
- Jordan, D. S., and W. A. Bone, decomposition of hydrocarbons at high temperatures, 7
union of carbon and hydrogen, 6
- Jerwitz's fat-extraction apparatus, 47
- Jones, H. O., displacement of benzyl by methyl in substituted nitrogen compounds, 276
H. C., dissociating power of different solvents, 95, 106, 135, 146, 159
- Journiaux, M., action of silver on hydrobromic acid, 94
of solar radiation on chloride of silver in presence of hydrogen, 36
- Jowett, H. A. D., constitution of pilocarpine, 274
new synthesis of α -ethyltricarballic acid, 274
- Juice, gastric, free hydrochloric acid in, 243
- Juices, vegetable, freezing-point, 234
- Juritz, C. F., South African College, 71
- KERN**, E. F., quantitative separation and determination of uranium, 224, 236, 251, 260, 271, 283
- Ketone, dibenzyl, condensation of benzil with, 264
- King's College, 110
- Kipping, F. S., and G. Clarke, amidomethylhydrindene, 22
- Kling, A., oxidation of propylglycol by *Mycoderma aceti*, 84
- Knight, J., and J. Adams, "The Self-educator in Chemistry" (review), 134
- Koettnitz, C., and D. Vorländer, formation of indigo from malonic ether of anthranilic acid, 243
- "**LABORATORY Companion** for use with Shenstone's *Inorganic Chemistry*" (review), 231
instruction, 122
- Lacombe, H., and G. Urbain, new volatile salt of beryllium, 304
- Lancaster, Storey Institute, 124
- Landauer, J., and J. Taylor, "Blowpipe Analysis" (review), 267
- Larter, A. T., displacement of alkyls from phenols by nitration, 23
- Laws, S. C., and E. H. Barton, air pressures used in playing brass instruments, 302
- Laycock, W. F., W. M. Gardner, and C. Rawson, "A Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing" (review), 255
- Le Sueur, H. R., and A. W. Crossley, substituted dihydrobenzenes, 300
- Lead, action of waters from Setif on, 243
ferrocyanide, 170
peroxide, aluminium persulphate as substitute for in colorimetric estimation of manganese, 239
- Leaf of a plant, distribution of acidity in, 208
- Lean, G., and W. C. Anderson, aluminium-tin alloys, 163
- Leeds Technical School, 124
- Lees, F. H., and F. B. Power, constituents of essential oil of *Asarum canadense*, 286
- Lefevre, L., and E. Grimaux, new colouring-matters, 12
- Leffmann, H., and W. Beam, "Select Methods in Food Analysis" (review), 218
- Lehldt, R. A., voltmeter for small currents, 240
- Leidie and Quennessen, MM., estimation of platinum and iridium in platinum ores, 2, 6
- Lespieux, R., bromated malonic dialdehyde, 219
- Leteur, F., action of sulphuretted hydrogen on acetylacetone, 60
- Letts, Prof., and R. F. Blake, chemical and biological changes during treatment of sewage by bacteria beds, 161
and J. Hawthorne, absorption of ammonia from polluted sea-water by *Ulva latissima*, 176
- Lewkowitch, J., theory of saponification, 243
- Light, movement of small suspended particles by influence of, 174
- Limettin, constitution, 288
- Limpach, L., and W. R. Hodgkinson, relations between physical constants and constitution in benzenoid amines, 221
- Lithium-ammonium, decomposition by ammonium chloride, 263
- Living, G. D., and J. Dewar, separation of least volatile gases of atmospheric air, and their spectra, 37, 51
- Liverpool, University College, 116
- London, City and Guilds Institute, 122
City College, 123
University, 109
water supply, 30, 94, 144, 190, 251, 311
- Lotus arabicus, poison of, 26
- Lowry, T. M., and H. E. Armstrong, bromocamphor, 300
derivatives of bromocamphor, 288
stereoisomeric and sulphonic derivatives of camphor, 22
- Lumière, A., and L., and F. Perrin, glycerophosphorus acid and glycerophosphites, 242
- Lumsden, J. S., and J. Walker, hydrobromides of undecylenic acid, 263
normal decanedicarboxylic acid, 263
- Lunge, G., "Coal-tar and Ammonia" (review), 230
and J. Bebie, contributions to science of nitrocellulose, 30, 41, 55, 66, 76, 90, 100, 133, 144, 153, 166, 178, 189, 200
- Lyle, T. R., circular filaments or circular magnetic shells equivalent to circular coils, and equivalent radius of a coil, 301
- McCRAE**, J., ethyl sec-octyl tartrate and its dibenzoyl and diacetyl derivatives, 263
and H. M. Dawson, metal-ammonia compounds in aqueous solution, 21
- M'Intosh, J. G., "The Chemical Essays of Charles William Scheele" (review), 255
estimation of ammonia in its salts, 10
of carbon in metals, 46
- M'Kenna, A. G., analysis of tungsten and chrome steels, 75
- McKenzie, A., esterification of nitrophthalic acid, 263
optically active hydroxybutyric acids, 287
- Magnesium aluminate, 222
- Magnetic field, behaviour of oxy-haemoglobin, carbonic-oxide-haemoglobin, methaemoglobin and derivatives in, 85
- Maihe, A., action of cupric hydrate on solutions of metallic salts, 96
of mercuric oxide on aqueous solutions of metallic salts, 36
- Maitland, W., and F. R. Japp, formation of carbazoles, 20
- Maldes and Massol, MM., solubility of mixtures of copper sulphate and sodium sulphate, 96
- Malmejac, Dr., action of waters from Setif on lead, 243
- Manchester, Institute of Public Health and Technology, 124
Municipal Technical School, 124
Owens College, 118
- Manchot, W., and J. Herzog, action of oxygen gas on cobaltocyanide of potassium and on chromous salts, 243
- Manganese dioxide and sulphuric acid, oxidation of benzinic carbides by, 242
estimation, 209, 247, 248, 269, 302
ammonium persulphate as substitute for lead peroxide in, 239
in water, 183, 278
- Manures, phosphatic, solubility in organic acids, 199
- Mauring, influence on chemical composition of potatoes, 258
- Maquene, L., and G. Bertrand, active erythrite, 11
racemic erythrite, 36
- March, F., action of bromacetophenone on sodium acetylacetone, 47
- Marckwald, W., radium, 190
- Marie, C., action of hypophosphorous acid on acetone, 83
dioxisopropylhypophosphorous acid, 292
- Martin, G., place of hydrogen in periodic system, 154
possible method of attaining absolute zero of temperature, 73
theory of chemical combination, 9
- Martindale, W., and W. W. Westcott, "The Extra Pharmacopœia" (review), 290
- Martine, C., action of benzoic aldehyde on sodium menthol, 47
- Masvol, G., acidimetric value of parasulphanilic acid, 36
thermic data relative to orthomonoiodobenzoic acid, 12
orthomonochlorobenzoic acid, 12
and M. Males, solubility of mixtures of copper sulphate and sodium sulphate, 96
- Materials, International Association for testing, 147
- Matignon, C., chloride of neodymium, 97
- Matthews, J. M., and A. H. Allen, "Commercial Organic Analysis" (review), 184
- Meldola, R., and J. V. Eyre, dinitro-orthoanisidine, 263
- Meldrum, A. N., and F. R. Japp, homologues of anhydrazetone-benzil, 19
- Mellon, W. W., Dr. Jerwitz's fat-extraction apparatus, 47
- Membranes, osmotic, preparation by electrolysis, 104
- Menthol, sodium, action of benzoic aldehyde on, 47
- Menthone, benzylidene, preparation, 47
- Merchant Venturers' Technical College, Bristol, 114
- Metal-ammonia compounds in aqueous solution, 21
- Metals, alkaline earth, solutions of salts of, 21
at high temperatures, action of ammonia on, 264
estimation of carbon in, 23
halides of, compounds of methyl sulphide with, 68, 79
minute structure of, 163
rare earth, place among elements, 245
- Metallic hydrate, action on solutions of salts of other metals, 36
- Metallurgy and mining, subject-matter index of, 2, 2
- Meteorite stones which fell near Zomba, British Central Africa, on Jan. 25, 1899, 4, 16, 34, 44, 65, 81, 91, 103
- Methaemoglobin, behaviour in magnetic field, 85
- Methanal, action of acid chlorides on, 60
- Methyl dimethylacetoacetate, action of nitric acid on, 276
in displacement of benzyl by, in substituted nitrogen compounds, 276
iodide of, and methylic alcohol, molecular combination formed by, 231
sodacetylacetates, action of acid chlorides on, 292
- Methylbenzazonine, pharmacology of, 38
butyrylacetate, decompositions, 72
- Metzger, F. J., and H. L. Wells, caesium-antimonious fluorides, and other double halides of antimony, 194
separation of tungstic and silicic acids, 3
- Meulen, H. T., contribution to our knowledge of indican, 250
- Meunier, J., estimation of free hydrochloric acid in gastric juice, 243

- Meunier, J., molecular combination formed by iodide of methyl and methylic alcohol, 231
- Meyer, F., compounds of gold with chlorine, 291
- Michie, A. C., and F. R. Japp, reduction of dibenzoylpropane and dibenzoyldiphenylbutadiene, 19
- Miller, E. H., and H. Fisher, lead and cadmium ferrocyanides, 170
- and R. W. Page, quantitative determination of cadmium, 312
- Minguin, J., and A. Haller, derivatives of benzylcamphor and of benzylidene camphor, 59
- Mining and metallurgy, subject-matter index of, 292
- Model which imitates behaviour of dielectrics, 240
- Modulus, Young's, measurement, 267
- Mohawkite, 29
- Moissan, H., action of ammonium metal on sulphuretted hydrogen, 279
- ammonium amalgam, 291
- decomposition of calcium-ammonium and of lithium-ammonium by ammonium chloride, 263
- electrolysis of ammonium chloride dissolved in liquefied ammonia, 256
- new method of manipulating gases liquefied in sealed tubes, 279
- new treatment of niobite, 47
- Molecular weights, value at temperature of ebullition, 146
- Molybdenum and aluminium, alloys of, 96
- Monazite from New Granada, 175
- "Mordants, Dyes, and other Compounds used in Dyeing and Calico Printing, a Dictionary of" (review), 255
- Morgan, G. T., influence of substitution on formation of diazamines and aminoazo-compounds, 297
- L. P., and E. F. Smith, chalcocypite, 29
- Morris, G. H., combined action of diastase and yeast on starch granules, 21
- Morse, H. N., and D. W. Horn, preparation of osmotic membranes by electrolysis, 104
- Moureu, C., and R. Delange, synthesis of acetylenic aldehydes, 60
- Mulliken, S. P., J. W. Brown, and P. K. French, importance of formic aldehyde as product of partial combustion of organic compounds, 15
- Muthmann, W., and E. Schroder, selenocyanic compounds, 223
- and L. Stutzel, ceric sulphates, 232
- NATURALISTS and Doctors of Medicine, Russian, Congress, 210**
- Neodymium chloride, 97
- Neutralisation, 11
- New Granada, monazite from, 175
- Newcastle-on-Tyne, Durham College of Science, 117
- Nichols, H. W., test for chloirine, 43
- Nicholson, H., utilisation of nascent carbon dioxide as a chemical reagent, 164
- Nickel and cobalt, separation by electrolytic method, 24
- flame colouration of, 291
- variation with temperature of thermo-electromotive force and electric resistance of, 217
- Nicolardot, P., separation of iron, 256
- Niobite, new treatment, 47
- Niobium, fused, preparation and properties, 47
- Nitrate, silver, 24
- Nitrile-phenols, synthesis and properties, 232
- Nitrosulphates, 7
- Nitrocellulose, 202
- science of, 30, 41, 55, 66, 76, 93, 100, 133, 144, 153, 166, 178, 189, 200
- "Nitrocellulose, Smokeless Powder, and Theory of Cellulose Molecule" (review), 218
- Nitrogen compounds, substituted, displacement of benzyl by methyl in, 276
- iodide of, 244
- peroxide, liquid, as a solvent, 275
- Nitromannite, 202
- Nitrometer work, 83
- Nitrotolyl-hydrazine, derivatives, 263
- Nitrourea, electrolytic reduction, 274
- Northampton Institute, 124
- Northam Polytechnic Institute, 124
- Norton, J. T., action of sodium thiosulphate on solutions of metallic salts at high temperatures and pressures, 254, 261
- Nottingham, University College, 118
- O'CONNOR, H., "The Gas Engineer's Pocket Book" (review), 242
- Ogawa, M., and E. Divers, ammonium and other imido-sulphites, 6
- Oil, essential, of Asarum canadense, constituents of, 286
- lemon, two new substances in, 9
- "Oils, Colours, and Varnishes, Painters'" (review), 277
- "Oils, Essential, Notes on" (review), 255
- Omeliarsky, V., fermentation of cellulose, 220
- Ores, gold, assaying of complex, 62, 74, 89, 98, 134
- platinum, estimation of platinum and iridium in, 216
- Organic compounds, importance of formic aldehyde as product of partial combustion of, 15
- Orton, K. J. P., benzylation of fatty acids in presence of ammonia, 274
- formation of amides, 274
- Oxford University, 110
- Oxide, action on solutions of salts of other metals, 36
- cerium, crystallisation of, 96
- preparation of pure, 84
- ferric, and alumina, mutual action at incipient white heat, 305
- mercuric, action on aqueous solutions of metallic salts, 36
- phosphorous, preparation, 36
- Oxides, metallic, oxidation of sulphurous acid to dithionic acid by, 287
- Oxygen, free, and potassium pyrogallate, heat evolved during reaction between, 256
- Oxy-haemoglobin, behaviour in magnetic field, 85
- Owens College, Manchester, 118
- Ozone, density and molecular weight, 33
- estimation, 232
- formation, 279
- PAGE, F. J. M., Chemical Society, 291
- R. W., and E. H. Miller, quantitative determination of cadmium, 312
- "Painters' Colours, Oils, and Varnishes" (review), 277
- "Paints and Painting, The Chemistry of" (review), 277
- Paper-making, chemical treatment of rags for, 257
- Paraffins in leaf of tobacco, 9
- Particles, small suspended, movement by influence of light, 174
- Pelabon, H., verification of a law of mechanical chemistry, 11
- Pentaerythrite, nitric derivatives of, 231
- Perin, F., and A. and L. Lumière, glycerophosphoric acid and glycerophosphites, 242
- "Periodic Classification and the Problem of Chemical Evolution" (review), 196
- Periodic system, place of hydrogen in, 154
- Perkin, F. M., "Qualitative Chemical Analysis, Organic and Inorganic" (review), 276
- W. H., action of nitric acid on methyl dimethyl-acetoacetate, 276
- "Petroleum, Handbook on, for Inspectors under the Petroleum Acts" (review), 250
- Pharmaceutical Society of Great Britain, School, 112
- "Pharmacopœia, the Extra" (review), 290
- Phenols, condensation with esters of acetylene series, 263
- displacement of alkyls from by nitration, 23
- Phenylhydrazine, urea from, action of saccharine on, 232
- Phillips, F. C., compounds of methyl sulphide with halides of metals, 68, 79
- "Philosophy, Chemical, Introduction to the Study of" (review), 278
- Phipson, T. L., analysis of a Silurian limestone rock, 283
- atomic weights, 2
- chemical names in botany, 183
- "Researches on the Past and Present History of the Earth's Atmosphere" (review), 277
- Phosphate, dibasic sodium, 24
- Phosphates in potable waters, determination, 69, 78
- insoluble, formation, 24
- manganic, 60
- Phosphorus chlorides, action on aromatic ethers of glycerin, 264
- estimation in basic steel, 108
- suboxide, 300
- non-existence, 264
- sulphochloride of, action on aromatic amines, 48
- Photographs of moving object, possibility of systematic error in, 163
- Physical Society, 10, 217, 240, 266, 301
- Pilocarpine, constitution, 274
- Pinacone and derivatives, isomerisations of, 268
- Piccol, constitution, 268
- Pipette, calibrating mercury, 21
- Pitchblende, estimation of uranium in, 283
- Plant food in soils, determination of available by use of dilute solvents, 298
- stem, leaf, and flower of, distribution of acidity in, 208
- Plants, mechanism of etherification in, 147
- Plates, sensitive, producing ultraviolet, 32, 40, 54, 67, 77
- Platinum in platinum ores, 216
- Plymen, F. J., and A. D. Hall, determination of available plant food in soils by use of dilute solvents, 298
- Poison of Lotus arabicus, 26
- Ponsot, A., limit of chemical reactions and that of product PV in gases, 242
- Pope, F. G., and J. M. Hird, derivatives of nitrotolylhydrazine, 263
- Potassium cobalticyanide, action of oxygen gas on, 243
- Potassium metabisulphite, 208
- perselenate, 2
- pyrogallate and free oxygen, heat evolved during reaction between, 256
- Potatoes, influence of manuring on chemical composition, 258
- Pouret, C., action of bromide of aluminium on acyclic chlorised hydrocarbons, 12
- "Powder, Smokeless, Nitrocellulose, and Theory of Cellulose Molecule" (review), 218
- Power, F. B., and F. H. Lees, constituents of essential oil of Asarum canadense, 286
- and F. Shedden, derivatives of gallic acid, 299
- Propylglycol, oxidation by Mycoderma aceti, 84
- Pseudoconitine, pharmacology of, 27
- Pyraconitine, pharmacology of, 38
- Pyridic bases, action on tetrahalogen benzoquinones, 72, 84
- Pyruvate and homoallantoic acid, 231
- Q** MINIMUM value of total heat of combination, 256
- Queen's College, Belfast, 121
- Cork, 122
- Galway, 122
- Quennessen and Leidie, MM., estimation of platinum and iridium in platinum ores, 216
- Quincke, G., clearing of turbid solutions, and movement of small suspended particles by influence of light, 174
- Quinine, basic saccharinate of, 232
- Quinones, tetrahalogen, action of pyridic bases on, 242, 316
- R**ADIATION, solar, action on chloride of silver in presence of hydrogen, 36
- Radicles, acetylo-metallic, 35
- Radio-activity, induced, produced by salts of radium, 25, 88, 316
- Radium, 190
- chemical reactions due to, 256
- rays emitted by, chemical effects produced by, 268
- salts of, induced radio-activity produced by, 25, 88, 316
- Radius, equivalent of, a coil, 301
- Rags for paper-making, chemical treatment, 257
- Rainfall, inverse relation of chlorine to, 176
- Ramage, H., volumetric estimation of manganese, 209, 269
- Ramsay, W., supposed formation of an oxide of hydrogen higher than the dioxide, 273
- Rankin, D. J., "Prospecting for Gold" (review), 290
- Rawson, C., W. H. Gardner, and W. F. Laycock, "A Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico Printing" (review), 255
- Rays emitted by radium, chemical effects produced by, 263
- Reaction, chemical, in which one of the products continues the same reaction, 263
- Reagent, chemical, nascent carbon dioxide as, 164
- Recoura, A., action of a metallic hydrate on solutions of salts of other metals, 11
- Redruth School of Mines, 124
- Redwood, B., and Capt. J. H. Thomson, "Handbook on Petroleum for Inspectors under the Petroleum Acts" (review), 230
- "Report of Her Majesty's Inspectors of Explosives, Annual" (review), 290

- "Report on Alkali, &c., Works" (review), 277
- Resins, sandarac, constituents, 263
- Reychler, A., oxides of chlorine, 234
- peroxide of chlorine as a sterilising agent for potable waters, 316
- Rhamnite, nitrated derivatives, 242
- Richard, A., electrolytic preparation of halogen compounds of acetones, 304
- Richards, Ellen H., "The Cost of Food" (review), 241
- J. W., abridgments in chemical calculations, 201
- blowpipe tests, 13
- measurement of gold and silver buttons in quantitative blowpipe assays, 181, 192
- mohawkite, 29
- T. W., and F. R. Fraprie, solubility of manganous sulphate, 156
- Rideal, S., humus and irreducible residue in bacterial treatment of sewage, 149
- sulphuric acid as a typhoid disinfectant, 161
- Ridenour, W. E., chemistry of deposits in steam boilers, 191
- estimation of hydrate in presence of alkali carbonate, 202
- Robertson, W., and M. O. Forster, halogen derivatives of *p*-cymene from substituted nitroamphanes, 8
- Rock, Silurian limestone, analysis, 283
- Rowland, F., reactions of hydration, 292
- Rosenheim, A., and R. Cohn, double metallic thiocyanates, 243
- Rowland, S., and A. Harden, autofermentation and liquefaction of pressed yeast, 64
- Royal Agricultural College, Cirencester, 115
- College of Science and Royal School of Mines, 111
- Dublin, 122
- Institution, 122, 220, 243, 279, 280
- Rücker, A. W., Address to British Association, 125
- Rudolph, P., and W. Autenrieth, action of sulphochloride of phosphorus on aromatic amines, 48
- Rudorf, G., "The Periodic Classification and the Problem of Chemical Evolution" (review), 196
- Ruhemann, S., and E. Wragg, condensation of phenols with esters of acetylene series, 263
- Runyan, E. G., indicator for determining total acidity of wines, 64
- Russell, E. J., and A. D. Hall, determining small quantities of carbonates, 299
- Russian Naturalists and Doctors of Medicine, Congress, 210
- SABATIER, P.**, action of an oxide or metallic hydrate on solutions of salts of other metals, 36
- and J. B. Senderens, preparation of aniline and analogous alkalis, 108
- Saccharine, action on urea from phenylhydrazine, 232
- St. Andrew's University, 121
- St. Paul's Cathedral, incrustation from stone gallery, 275
- Sakurai, J., chemical education, 151
- Salford Technical Institute, 124
- Salt, circulation, 56
- separation and formation of oceanic salt deposits, equilibrium law as applied to, 177
- Salts, amine, action of bases and acids on, 36
- Salts, basic, containing two metals, 11
- chromous, action of oxygen gas on, 243
- metallic, action of cupric hydrate on solutions of, 96
- mercuric oxide on aqueous solutions of, 36
- sodium thiosulphate on solutions of at high temperatures and pressures, 254, 261
- radium, radio-activity of, 88
- Saponification theory, 243
- Saps, vegetable, freezing-point, 234
- "Scheele, Charles William, The Chemical Essays of" (review), 255
- Schroder, E., and W. Muthmann, selenocyanic compounds, 223
- Schumann, V., producing ultraviolet sensitive plates, 32, 40, 54, 67, 77
- Sea-water, polluted, absorption of ammonia from by *Ulva latissima*, 176
- Selenite, dehydration, 289
- Selenocyanic compounds, 223
- Semenov, J., nature of X rays, 83
- Senderens, J. B., and P. Sabatier, preparation of aniline and analogous alkalis, 108
- Setif, waters of, action on lead, 243
- Sewage, bacterial treatment, humus and irreducible residue in, 149
- treatment by bacteria beds, chemical and biological changes during, 161
- Seyewetz, A., and M. Blanc, colourless compound of sodium tetratoxylsulphite with ethylalphathylamine and its transformation into a colouring matter, 47
- Shedden, F., and F. B. Power, derivatives of gallic acid, 299
- Sheffield, University College, 119
- Shells, magnetic circular, equivalent to circular coils, 301
- Shenstone, W. A., "Laboratory Companion for use with Shenstone's Inorganic Chemistry" (review), 231
- Shepard, C. H., nitrometer work, 83
- W. K., new solution for copper voltameter, 226
- Silica, separation of tungstic acid from, 75
- Silicates, natural, alkaline reactions of, 312
- Silico-vanadio-molybdates, 295
- Silver, action on hydrobromic acid, 94
- and gold buttons in blowpipe assays, 181, 192
- chloride, action of hydrogen peroxide on, 231
- solar radiation on, in presence of hydrogen, 36
- Simon, L. J., action of urea on pyruvic acid, 231
- urethane on pyruvic acid, 219
- Smith, A., nomenclature of the ions, 279
- E. A., assaying of complex gold ores, 62, 74, 89, 98, 134
- E. F., and L. P. Morgan, chalcopyrite, 29
- Society of Arts Examinations, 153
- Soda, solid, thermic examination of hydrates of, 84
- Sodacetylacetates, methyl and ethyl, action of acid chlorides on, 292
- Sodium acetylacetone, action of bromacetophenone on, 47
- sulphate and copper sulphate, solubility of mixtures of, 96
- tetratoxylsulphite, colourless compound of with ethylalphathylamine, 47
- thiosulphate, action on solutions of metallic salts at high temperatures and pressures, 254, 261
- Soils, determination of available plant food in by use of dilute solvents, 298
- Solutions, concentrated, catalysis in, 205, 213
- turbid, clearing of, 174
- Solvents, dissociating power of different, 95, 106, 135, 145, 159
- South African College, 71
- South-Eastern Agricultural College, 124
- South-Western Polytechnic, 123
- Spectroscopies, multiple transmission fixed-arm, 266
- Spectrum of cyanogen, 10
- Spelling, American v. English, 10
- Sperber, J., "Leitfaden für den Unterricht in der Anorganischen Chemie" (review), 291
- Sprankling, C. H. G., and W. A. Bone, bromination of trimethylsuccinic acid and interaction of bromotrimethylsuccinate and ethyl sodiocyanacetate, 399
- synthesis of alkyl-substituted tricarballic acids, 287
- Starch granules, combined action of diastase and yeast on, 21
- Steel, basic, estimation of phosphorus in, 108
- works analysis, bibliography, 249
- Steele, B. D., place of rare earth metals among elements, 245
- Steels, chrome, analysis, 75
- Stem of a plant, distribution of acidity in, 208
- Sterba, J., crystallisation of cerium oxide, 96
- preparation of pure cerium oxide, 84
- Stevens, H. P., hydrochloride of thiocarbamide, 286
- Stillman, T. B., "Engineering Chemistry" (review), 315
- Stone gallery of St. Paul's Cathedral, incrustation from, 275
- Storey Institute, Lancaster, 124
- Stutzel, L., and W. Muthmann, ceric sulphates, 232
- Substitution derivatives, part played by residual affinity in formation, 301
- Sugars from cellulose, 7
- Sulphate, cupri-ammonia, influence of temperature on dissociation of, 21
- manganous, solubility, 156
- Sulphates, ceric, 232
- Sulphide, methyl, compounds with halides of metals, 68, 79
- Sulphur, orienting influence of, 301
- Superphosphates, manufacture, utilisation of fluoric gases formed in, 222
- Sutherst, W. F., freezing-point of vegetable saps and juices, 234
- influence of manuring on chemical composition of potatoes, 258
- solubility of phosphatic manure in organic acids, 199
- Syers, H. W., and E. C. C. Baly, spectrum of cyanogen, 10
- Syntheses by molecules containing methylene group associated with negative radicles, 24
- TAKA-DIASTASE, 23**
- Tarbouriech, J., and A. Astruc, acidimetry of arsenic acid, 47
- Tartrate, ethyl sec-octyl, and its dibenzoyl and diacetyl derivatives, 263
- Taylor, J., and J. Landauer, "Blowpipe Analysis" (review), 267
- Temperature, absolute zero of, possible method of attaining, 73
- nadir of, 49
- Tervet, J. N., and J. T. Hewitt, action of bromine on three toluene azophenols, 19
- Textiles, bleaching, electrolysis in, 156
- Thallium chlorobromides of type Tl_2X_6 , 268
- Thibault, P., new crystallised salicylate of bismuth, 310
- Thiocarbamide, hydrochloride of, 286
- Thiocyanates, metallic, double, 243
- Thomas, V., chlorobromides of thallium of type Tl_2X_6 , 268
- thallium chlorobromides, 24
- Thomson, Capt. J. H., and B. Redwood, "Handbook on Petroleum for Inspectors under the Petroleum Acts" (review), 230
- W., detection and estimation of arsenic in beer and articles of food, 173
- Thorium, new element associated with, 179, 187, 219
- Thorpe, T. E., and J. Holmes, paraffins in leaf of tobacco, 9
- Thymol, 23
- Tilden, W. A., "Introduction to the Study of Chemical Philosophy" (review), 278
- and H. Burrows, constitution of limetin, 288
- Tin-aluminium alloys, 316
- Tintometer in water analysis, 59
- Titanium, estimating, warning against use of fluoriferous hydrogen peroxide in, 311
- Tobacco, leaf, paraffins in, 9
- Trillat, A., action of contact on secondary and tertiary alcohols, 60
- oxidation of non-saturated alcohols by action of contact, 292
- preparation of vanilline, 292
- Trinitrobenzene, reduction with hydrogen sulphide, 287
- Trinitrotoluene, reduction with hydrogen sulphide, 287
- Trioxymethylene, action of benzoyl chloride on, 147
- Triphenylchloromethane, 14
- Tungsten, analysis, 75
- Typhoid, sulphuric acid as a disinfectant, 161
- ULVA latissima**, absorption of ammonia from polluted seawater by, 176
- Umbgrove, H., and A. Haller, tetrachlorised dimethyl and diethylamidobenzoylbenzoic acids and derivatives, 232
- U.S. Patent Office, system of indexing chemical literature adopted by, 203, 210
- Universities, 109
- University College, 111
- Bristol, 113
- Dundee, 119
- Liverpool, 116
- Nottingham, 118
- Sheffield, 119
- of North Wales, 113
- of South Wales and Monmouthshire, 113
- of Wales, 112
- of Aberdeen, 120
- Birmingham, 114
- Cambridge, 110
- Dublin, 110
- Edinburgh, 120
- London, 109
- Oxford, 110
- St. Andrews, 121
- Tutorial College, 124
- Uranium, experiments with, 83
- in pitchblende, estimation, 283
- separation and determination, 224, 236, 251, 260, 271, 283
- Urea, action on pyruvic acid, 231
- from phenylhydrazine, action of saccharine on, 232
- Urban G., and H. Lacombe, new volatile salt of beryllium, 304
- Urethane, action on pyruvic acid, 219

- VAILLANT, G.**, colour of ions, 146
Vanilline, preparation, 292
"Varnishes, Colours, and Oils, Painters," (review), 277
Vegetable saps and juices, freezing-point, 234
Vegetables, acids in, 208
Vespignani, G. B., and **G. Carara**, energy of some metallic hydrates, deduced from hydrolysis of the salts, 280
Victoria University, 115, 118
Vignon, L., and **F. Gerin**, nitrated derivatives of arabite and rhamnite, constitution of nitric ethers, 242
nitric derivatives of pentaerythrite, 231
nitromannite and nitrocellulose, 202
reducing properties of nitric ethers, 219
Volatilisation of elements, calculation of heat of, 208
Voltmeter, copper, new solution for, 226
Voltmeter for small currents, 240
Von Knorre, G., and **K. Arndt**, oxidation of hydroxylamine, 220
Vorlander, D., and **C. Koettwitz**, formation of indigo from malonic ether of anthranilic acid, 243
WADE, E. B. H., new hygrometric method, 302
Wales, North, University College, 113
South, and Monmouthshire, University College, 113
University College, 112
Walker, G. W., asymmetry of Zeeman effect, 218
J., nomenclature of ions, 162
and J. S. Lumsden, hydrobromides of undecylenic acid, 263
normal decane-dicarboxylic acid, 263
Walters, H. E., ammonium persulphate as substitute for lead peroxide in colorimetric estimation of manganese, 239
Warth, H., mutual action of alumina and ferric oxide at incipient white heat, 305
analysis, tintometer in, 59
"characteristic" of, numerical value, 240
estimation of carbonic acid in, 80, 92, 101, 145, 158, 164
manganese in, 278
supply, London, 30, 94, 144, 190, 251, 311
Waters from Setif, action on lead, 243
manganese in, 183
potable, determination of phosphates in, 69, 78
potable, peroxide of chlorine as a sterilising agent for, 316
Watson, W. F., "Elementary Experimental Chemistry, Inorganic" (review), 229
Weight, molecular, of chloral hydrate at temperature of ebullition, 184
Weights, molecular, value at temperature of ebullition, 146
Wells, H. L., purification of caesium material, 169
and F. J. Metzger, caesium-antimonious fluorides and other double halides of antimony, 194
separation of tungstic and silicic acids, 3
West Ham Municipal Institute, 124
Westcott, W. W., and **W. Martindale**, "The Extra Pharmacopœia" (review), 290
White, S. A. F., effect of high frequency oscillatory field on electrical resistance, 10
Wiesbaden, Chemical Laboratory, 108
Wines, acidity of, indicator for determining, 64
Withers, W. A., and **G. S. Fraps**, rate of nitrification of fertilisers, 45, 57
Wolverhampton Free Library Science and Technical School, 124
Woodman, A. G., and **L. L. Cayvan**, determination of phosphates in potable waters, 69, 78
Wragg, E., and **S. Ruhemann**, condensation of phenols with esters of acetylene series, 263
X-RAYS, nature of, 83
Xanthenes, transformation of two xanthydrols into, 304
Xanthydrols, two, transformation into xanthenes, 304
YEAST and **diastase**, combined action on starch granules, 21
pressed, autofermentation and liquefaction of, 264
Yorkshire, chlorine in, 185
College, Leeds, 115
Young, A. V. E., "The Elementary Principles of Chemistry" (review), 302
Young's modulus, measurement, 267
ZAMANOS, D., and **E. Charon**, constitution of piceol, 268
Zeeman effect, asymmetry, 218
"Zella, Die Chemische Organisation der" (review), 315
Zero, absolute, of temperature, possible method of attaining, 73
Zunino, V., dehydration of selenite and hydration of anhydrite, 289

UNIVERSITY OF ILLINOIS-URBANA



3 0112 063431834